

Adsorption of Amine Compounds on the Au(111) surface – A Density Functional Study

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A Density Functional Theory study of the adsorption energetics of various amine compounds on the gold (111) surface revealed that preferential binding occurs in under-coordinated sites. The largest binding energy is obtained when a gold adatom is placed in the fcc position and the amine positioned with the nitrogen above the adatom. The results are compared with previous calculations for thiols, phosphines and ethynylbenzene molecules to provide a meaningful comparison within a consistent computational framework. The systematic increase in binding energy with methyl group substitution previously observed for phosphine compounds is not observed for the amine analogs. The binding energy of the amines is considerably lower than for thiols and binding is indicated for only the adatom geometry - a result consistent with experimental data.

KEYWORDS: density functional theory; surface adsorption; molecular electronics; adatom

1. Introduction

The development of techniques for forming and analyzing the now ubiquitous self-assembled monolayers (SAMs) on surfaces has enabled the measurement of electronic properties of single molecules. The field has grown substantially since Nuzzo and Allara first described alkanethiols adsorbed onto gold surfaces from solution¹. The most widely studied systems involve alkane thiols on gold² although conjugated aryl thiol and dithiol SAMs have been reported³. Reference 4 contains a thorough review of applications of such systems in the context of nanotechnology. The chemical stability of gold and its strong interaction with thiols makes it an ideal surface for studies of SAMs.

In contrast, studies of SAMs anchored to gold surfaces by groups other than thiols are sparse. Some examples of such investigations include work on diisocyanide monolayers⁵ and SAMs of ethynylbenzene on Au(111)⁶ while other acetylenes have also been shown to bond to gold surfaces⁷. The energetics and candidate geometries of the ethynylbenzene system were studied at a DFT level⁸. Other computational studies include the adsorption of ammonia⁹ and phosphine compounds¹⁰ on Au(111).

Recently, amine-bound SAMs have been used in molecular electronics experiments.¹¹⁻¹⁴ In one approach, a statistical analysis of thousands of STM conductance measurements was made, a technique that was originally applied to thiol molecules by Tao.¹⁵ Conductance histograms were compiled and the peaks indicate values corresponding to the conductance of a single molecule sandwiched between STM tip and substrate. The histograms were found to be very diffuse in the case of thiols^{12,14} making the extraction of the single-molecule conductance troublesome, unless a filtering algorithm is implemented.^{11,12,14,15} In contrast, the histograms resulting from measurements on amines yielded well-defined conductance values for single molecules.¹²⁻¹⁴ Venkataraman et al¹⁴ attribute this to the amine-Au bond being through the nitrogen lone-pair and relatively insensitive to the local structure. These authors also find, in DFT calculations, that butanediamine is bound in an upright position only to an Au adatom on the gold surface.

Bilic et al.⁹ characterized the ammonia-Au(111) interaction. Li and Kosov¹⁶ investigated the interaction of aniline with the Au(111) surface in a relaxed geometry as well as in a stretched junction. They find that, for geometries where the amine is in a perpendicular orientation relative to the surface (lending itself to

molecular junction formation), the aniline bonds preferentially in the atop geometry. They offered this as an explanation for the well-defined nature of the amine histograms in the experiments described above. However, they also find a large interaction energy with the nitrogen in the atop site and the phenyl ring lying flat on the surface.

Here we expand on this work by considering the adsorption of a series of amines (Figure 1) on Au(111). We also compare the present results for amines with our previous calculations of the binding energies of phosphines, thiols and ethynylbenzene on Au(111).

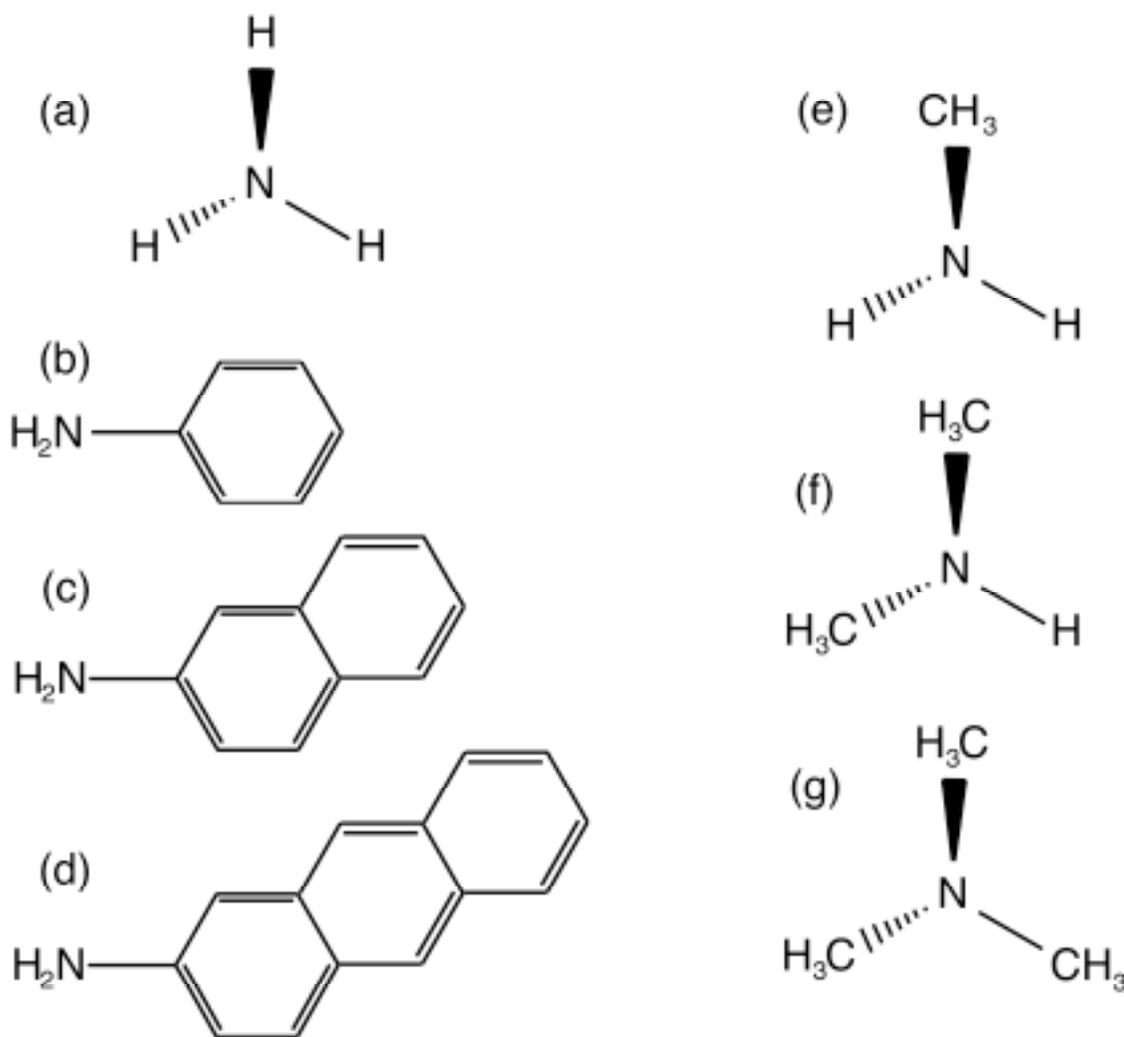


Figure 1: Amines investigated in this study: (a) ammonia – NH₃, (b) aniline – NH₂C₆H₅, (c) 2-aminonaphthalene – NH₂C₁₀H₇, (d) 2-aminoanthracene – NH₂C₁₄H₉, (e) methylamine – NH₂CH₃, (f) dimethylamine – NH(CH₃)₂ and (g) trimethylamine – N(CH₃)₃.

2. Methods

All the calculations in this paper were conducted using the SIESTA software package. This electronic structure code implements density functional theory within periodic boundary conditions and is based on the linear combination of atomic orbitals approximation.^{17,18} The valence electrons are described by atom-centered basis sets, and the nucleus/core electrons are represented by norm-conserving pseudopotentials. The orbitals are strictly localized in real-space, with a cut-off radius defined by a single energy shift parameter for all atoms that represents the energy increase in the orbitals due to confinement.

The code has been previously modified to allow coordinate input in a mixed Cartesian and Z-matrix internal coordinate format¹⁹, which is particularly convenient for studying molecules on surfaces²⁰.

For the calculations reported here, the generalized-gradient approximation (GGA) to the exchange-correlation functional due to Perdew, Burke and Ernzerhof (PBE)²¹ was used throughout. All calculations are spin unrestricted and employ a Fermi smearing of 25 meV to aid convergence. Norm-conserving pseudopotentials (with a relativistic correction in the case of Au) generated according to the scheme of Troullier and Martins²² were used. A double-zeta plus single polarization function was used to represent the 1s electrons in H, 2s and 2p electrons in C and 6s and 5d electrons in Au. An energy shift of 5 mRy was used in the confinement of the basis set and an effective kinetic energy cut-off for the real space integration grid of 300 Ry was employed. Transferability of the pseudopotentials and convergence with respect to the other parameters have been previously tested by comparison with well-known experimental results and all-electron calculations⁸.

The geometries of the isolated molecules were optimized using a conjugate gradients algorithm with the molecules described by Z-matrix coordinates. Only a single k-point in reciprocal space is required for calculations on the isolated molecules. Each molecule was placed in a cubic unit cell of either 10 or 20 Å to eliminate intermolecular interactions.

The gas-phase optimized molecules were then placed on an Au(111) surface. Conjugate gradients optimizations were performed with the molecule described in Z-matrix and the surface in Cartesian coordinates. For all but the large multiple-ring aromatic amines, the unit cell contained four Au(111)

surface layers with 3x3 gold atoms per layer, implying a 1/9 monolayer coverage. For the adsorbed and the isolated molecule optimizations, the geometry was taken to be minimized when all torques were below 0.0003 eV/degree and all forces below 0.02 eV/Å. A Monkhorst-Pack grid²³ of 5x5 k-points was used in the plane of the surface.

For each molecule, separate optimizations were performed in stages starting with the nitrogen atom fixed in one of five binding sites. Initially, the rest of the molecule as well as the height of the nitrogen above the surface were relaxed, while the gold atoms were fixed in their bulk positions. A final relaxation was then performed with no constraints. The ontop, bridge, fcc and hcp hollow binding sites were used as starting positions. In addition an “adatom” geometry was created where the nitrogen is placed in the ontop position above a gold adatom on the Au surface. The adatom was also allowed to relax, and both fcc and hcp adatom sites were used as starting points for the optimisations. Figure 2 shows the relaxed geometries for these five starting configurations for a selection of the amines.

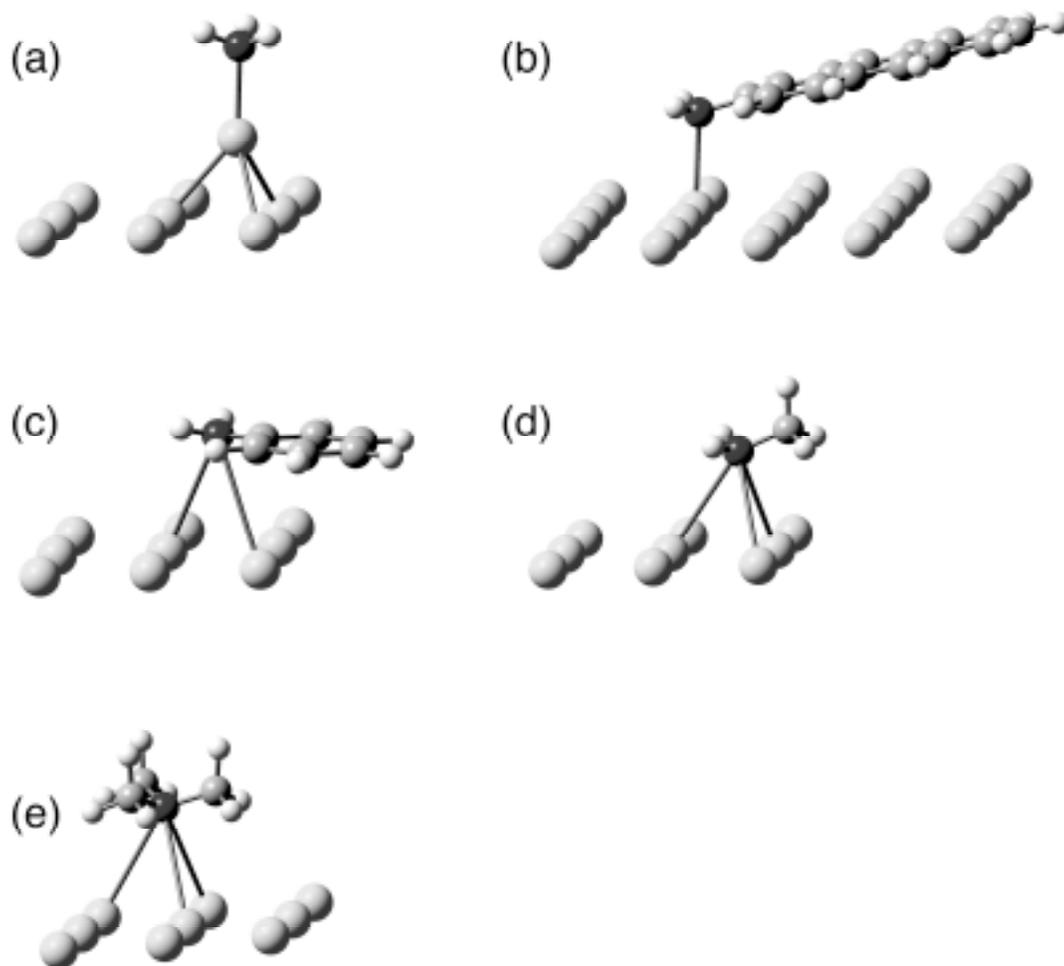


Figure 2: Some representative adsorption geometries of the amines on Au(111): (a) Ammonia with adatom geometry, (b) 2-aminoanthracene in ontop site, (c) aniline in bridge site, (d) methylamine in fcc site and (e) trimethylamine in hcp site.

In the case of 2-aminonaphthalene and 2-aminoanthracene, a BFGS optimization was performed with both molecule and slab described in Cartesian coordinates. The unit cell contained 4x4 and 5x5 gold atoms per layer for these two molecules respectively. Larger unit cells, in these cases, were necessary to ensure negligible interaction between these larger molecules and their periodic images. For these two molecules, only the ontop position was considered for nitrogen atom binding. In all cases interaction between the periodic images of the molecule in the unit cell was less than 0.005 eV.

In the case of the aromatic ligands, the optimization of molecular coordinates is troublesome when using the Z-matrix description. This is because the cyclic nature of the phenyl ring causes interdependencies in a Z-matrix coordinate system¹⁹. Thus, for aniline, in the initial constrained optimizations the phenyl ring was fixed in the gas-phase optimized structure, whereas the NH₂ component together with the rotation of the ring with respect to NH₂, was allowed to relax.

In all cases the final unconstrained optimizations were performed in Cartesian coordinates. The use of a Z-matrix input and optimization format is not strictly necessary in the present work although it does provide certain conveniences in setting up input geometries where a molecule is docked onto a particular substrate site.

Interaction energies were obtained by subtracting the energies of the substrate and molecule (in the fully optimized adsorbed geometries) from the total energy, but retaining the full basis set associated with the entire system. This constitutes the counterpoise correction²⁴ to the basis set superposition error (BSSE), which leads to an overestimation of binding energies. Although this method can sometimes overcorrect, it is expected to be reasonable for modest basis sets such as DZP. For the amine molecules studied here, it is also straightforward to calculate the full adsorption energy because no bond dissociation occurs and only the energy required to distort the molecule and substrate from their isolated geometry to the adsorbed geometry is required. Except in the ontop and adatom sites the interaction energy is small and little distortion of the molecule or slab occurs upon adsorption. For the ontop and adatom sites the distortion energies are of the order of 10 % of the interaction energies. In all cases, the distortion energies are, as

expected positive, and decrease the adsorption energy relative to the interaction energy. Below we report only the adsorption energies.

3. Results and Discussion

3.1 Amines adsorbed on Au(111)

Adsorption energies and heights of the nitrogen atom above the gold surface are summarized in Table 1. For the ontop, bridge, fcc and hcp sites heights were calculated by taking the average position of the surface Au atoms. The sites with high coordination (bridge, fcc, hcp) are unfavorable and produce negligible adsorption energies, $|E_i| < 0.1$ eV. Interaction strengths of this order of magnitude are probably below the level of reliability of the present calculations, indeed calculating such weak binding at any level of calculation is extremely difficult. The adsorption energies of the ontop site are larger but still weak with $0.1 < |E_i| < 0.3$ eV. Significant adsorption energies are observed only in the adatom geometry, $0.3 < |E_i| < 0.6$ eV. Placing the adatom in the hcp site and performing the same calculations gives adsorption energies that are less favorable for all molecules compared with the fcc site, however the energy difference is only of order 0.02 eV. Our result for the adatom adsorption energies are in good agreement with the estimated value of 0.5 eV for butanediamine from DFT calculations by Vankarataran et al.¹⁴

Site molecule	ontop		bridge		fcc		hcp		adatom	
	E_{ads}	h								
NH ₃	-0.21	2.45	-0.04	2.76	-0.03	2.90	-0.03	2.82	-0.47	2.35
NH ₂ C ₆ H ₅	-0.12	2.65	-0.02	3.21	-0.03	3.29	-0.04	3.29	-0.30	2.48
NH ₂ C ₁₀ H ₇	-0.11	2.76	-	-	-	-	-	-	-	-
NH ₂ C ₁₄ H ₉	-0.17	2.64	-	-	-	-	-	-	-	-
NH ₂ CH ₃	-0.29	2.46	-0.07	2.77	-0.07	2.81	-0.07	2.81	-0.53	2.37
NH(CH ₃) ₂	-0.29	2.55	-0.08	2.82	-0.08	2.82	-0.08	2.84	-0.53	2.40
N(CH ₃) ₃	-0.22	2.72	-0.07	3.00	-0.06	3.02	-0.06	3.02	-0.50	2.45

Table 1: Adsorption energies (eV), and binding heights (Å) of the nitrogen atom above the Au(111) surface.

As mentioned in the methods section the optimized geometry of the adsorbed molecule is close to the gas phase optimum geometry, interaction with the substrate is not strong in any of the adsorption sites and so little distortion of the molecule occurs upon adsorption. Orientation of the amine molecule is always with the nitrogen atom pointing towards the substrate, (Fig 2), presumably because the bond to the surface occurs through the nitrogen lone pair. All of the aliphatic amines are oriented perpendicular, or near-perpendicular to the surface with the three nitrogen-substituent bonds arranged symmetrically with respect to the surface, Figures 2(a), (d) and (e) illustrate this geometry. The molecular geometries differ only slightly between the various adsorption sites.

In a similar series of calculations for phosphine compounds¹⁰ we found that substitution of hydrogen atoms with methyl groups generally increases the adsorption energy, furthermore PH_3 was found to be unbound. The same trend is not observed for the amine compounds studied here. For example, the adsorption energy of trimethylamine in the ontop site is approximately the same as that of ammonia, but higher in the adatom geometry. Adsorption energies for dimethylamine and methylamine, while larger than ammonia, are the same for both ontop and adatom sites.

The aromatic amines are adsorbed with the ring substituents relatively flat to the surface. In the case of aniline the angle between the phenyl ring and the plane of the surface is 18.7° in the ontop geometry and 28.4° in the adatom geometry. The adsorption geometry of 2-aminonaphthalene in the ontop site is with the plane of the phenyl rings at an angle of 10° with the surface, while for 2-aminoanthracene this angle is 19° in the ontop site. The fact that the phenyl rings lie flat to the surface for these molecules suggests that part of the binding energy comes from interaction between the delocalized π -electrons on the aromatic ring and the gold surface. When the molecule is adsorbed onto an adatom this interaction with the surface is weaker and consequently the ring does not lie as flat to the surface.

Substitution of one of the hydrogen atoms of ammonia with phenyl, naphthyl or anthracenyl groups (see figure 1) leads to smaller adsorption energies compared with the methyl substituted amines by about a

factor or two. A possible explanation of this is the electron donating nature of the methyl substituents. We will return to this point in the following section where amine adsorption is compared with other adsorbates.

Increasing the size of the aromatic substituent from phenyl through to anthracenyl increases the adsorption energy (and interaction energy), although a clear trend of increasing adsorption with increasing size of the aromatic group is not clear from the available data. Phenyl and naphthyl groups give about the same adsorption energy. One might expect the adsorption energy to increase with increasing ring size if the aryl-gold bond is responsible for part of the interaction energy. To investigate this aspect, the adsorption energy of 2-aminoanthracene with the surface was calculated as a function of the angle of rotation of the aromatic group. The flat geometry is energetically favored for this molecule, as seen in Figure 3. The BSSE corrected potential energy surface is shallow with respect to the rotation. When the interaction energies are not corrected for BSSE however, a deeper PES is observed and the interaction energy of the flat geometry increases from -0.18 (at $\theta=5^\circ$) to -0.85 eV (at $\theta=-5^\circ$). Taking account of the BSSE is therefore seen to be essential for the present geometry. Furthermore, we do not observe any binding when $\theta > 45^\circ$.

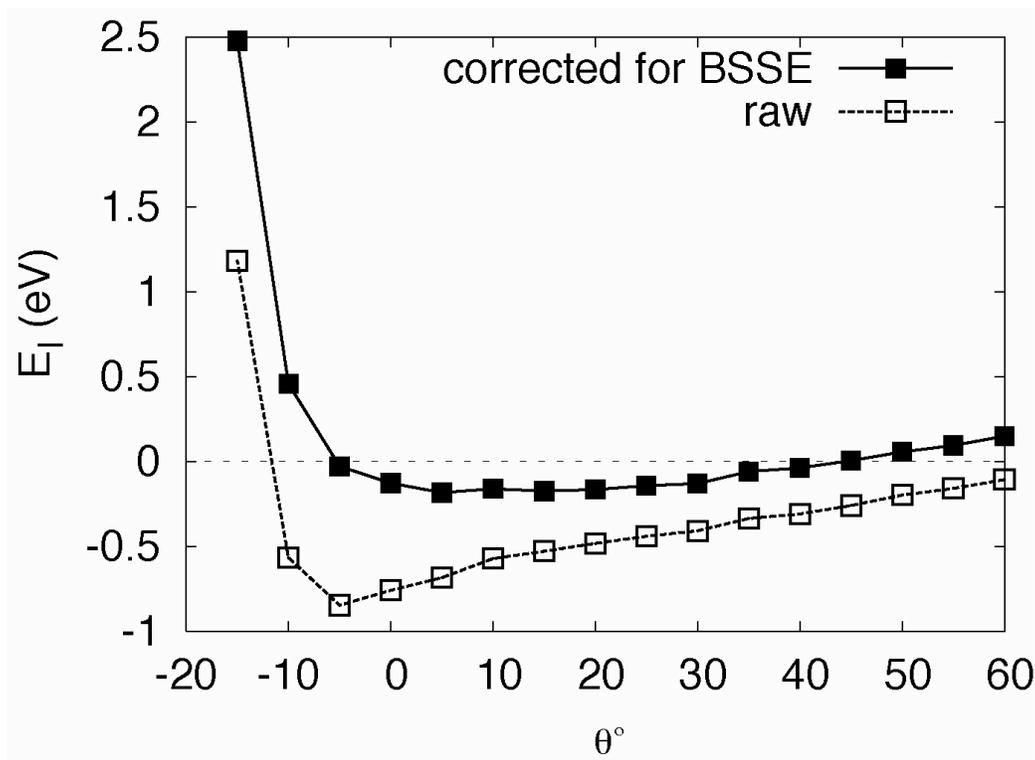


Figure 3: Raw and BSSE corrected adsorption energies of 2-aminoanthracene on Au(111) as the molecule is rotated with the aromatic group lying flat on the surface at $\theta=0^\circ$. The nitrogen is kept fixed at a height of 2.64 \AA in the ontop position above the surface.

Figure 4 shows the density of states (DOS) projected onto the 5d and 6s orbitals of the gold atom associated with the bond to the nitrogen atom in the ontop and adatom geometries compared with the same DOS in the absence of the adsorbate. Changes in the DOS reflect hybridization of the substrate and adsorbate orbitals and the degree of bonding that occurs upon adsorption. For the ontop site (Figs 4(a) and (c)) the DOS on both the 5d and 6s Au orbitals re-distributes when the ammonia molecule is adsorbed. The 5d orbital loses some density just below the Fermi energy and gains density about 5 eV below the Fermi energy, similarly the 6s orbital loses density about 1 eV below the Fermi energy and gains a small amount at about 5 eV below the Fermi energy. This redistribution of the available states and transfer of charge stabilizes the bond between the gold atom and ammonia molecule, although the degree of redistribution is relatively small leading to a relatively weak bond. A similar redistribution occurs for the adatom site although it is more pronounced, in particular a peak appears in both the 5d and 6s projected DOS at about 6 eV below the Fermi energy. This peak is quite sharp and more characteristic of a molecular orbital, it may therefore be due to mixing with orbitals associated with the ammonia adsorbate. In Figure 4(b) the onset of the edge of the valence band is shifted away from the Fermi energy when the ammonia molecule is adsorbed, this would indicate that electron charge is being transferred into the substrate upon adsorption. As we shall see in the discussion below this observation is supported by the Mulliken analysis which clearly shows a net positive charge on the ammonia adsorbate and negative charge on the Au substrate.

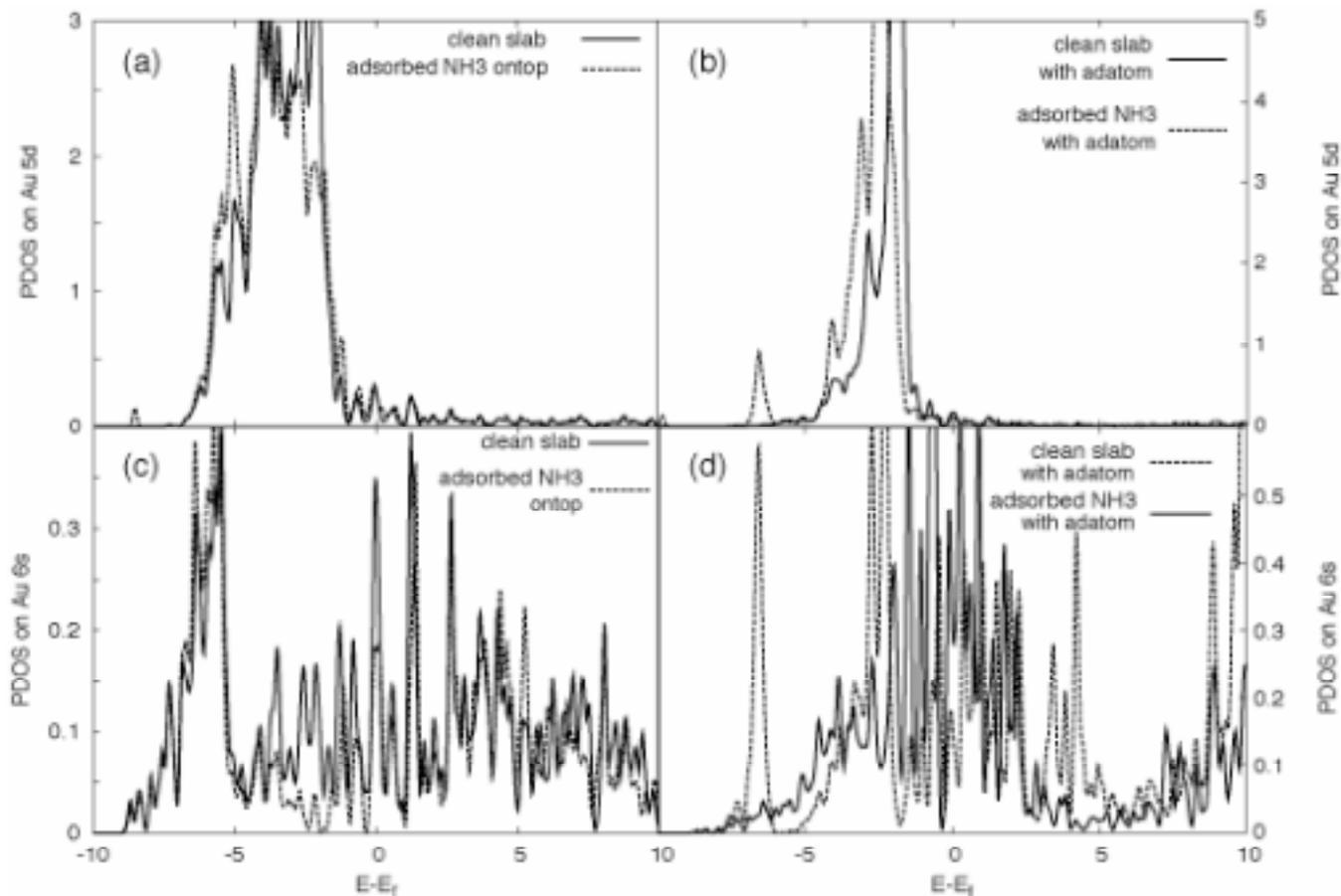


Figure 4: Density of states projected onto the orbitals of the gold atom bonded to the nitrogen. (a) 5d orbitals in ontop geometry, (b) 5d orbitals in adatom geometry, (c) 6s orbitals in ontop geometry, (d) 6s orbitals in adatom geometry.

Table 2 lists the Mulliken populations for the net charge on the ammonia molecule and the gold substrate as well as the population overlap between the nitrogen and nearest gold atoms in the bridge, ontop and adatom geometries. The adsorption energy follows the overlap and charge transfer populations, as both of these increase the strength of the amine-gold bond also increases. The overlap population is a measure of electron sharing between N and Au atoms, as this overlap increases the covalent character increases and the bond becomes stronger. It should be noted, however, that the overlap populations are relatively small. As the charge of the adsorbate and substrate increase then the electrostatic attraction between them will increase, again giving a stronger bond. In the adatom geometry, the overlap population is 0.082e and the charge transfer is 0.172 electrons from the ammonia to the gold surface. These values are small but not negligible and are responsible for the adsorption energy of -0.47 eV. In the ontop geometry, the overlap

population is 0.047e and the charge transfer 0.08 electrons from molecule to surface, consistent with the weaker adsorption energy. The adsorption energy of ammonia in the ontop site is -0.21 eV, comparable with the -0.33 eV obtained by Bilic et al⁹. The variation may be due to differences in basis set and exchange correlation potential – Bilic et al⁹ use a plane-wave basis with the PW91 exchange correlation functional.

Binding Site	Mulliken Charge		Mulliken Population
	Molecule	Substrate	Au-N Overlap
bridge	+0.042	-0.042	0.039
ontop	+0.084	-0.084	0.047
adatom	+0.172	-0.172	0.082

Table 2: Mulliken population analysis, in units of the electron charge, for ammonia adsorbed on the Au substrate in three binding sites. Mulliken charge of the molecule is the sum of atomic charges of the constituent atoms of the molecule with the molecule adsorbed on various sites of the Au substrate. Substrate Mulliken charge is total charge of Au substrate.

Table 3 demonstrates the effect of substituting one of the hydrogen atoms on the ammonia molecule with methyl and various aromatic groups. Mulliken populations are compared for the various molecules both in the gas phase and adsorbed in the ontop site. The total charges are broken down into the charge for the NH_2 portion of the molecules and for the substituents. As expected, for the gas phase molecules, substitution of a methyl group results in electron donation to the nitrogen atom compared with the phenyl rings (or a hydrogen atom) which are relatively electron withdrawing. Increasing the number of phenyl rings withdraws more charge from the NH_2 group. It is interesting to note that for the adsorbed molecules the NH_2 charge is about the same for the aromatic molecules but considerably more positive for ammonia and for methylamine. This provides a clue to the adsorption mechanism whereby donation of electron charge from the N atom into the surface is a key component. The total charge donated into the substrate is larger for two of the phenyl substituted amines compared with methylamine, despite the fact that the latter has a stronger bond by approximately a factor of two. Although bonding for the aromatic amines is

complicated by the interaction of the π -electrons one would not expect this to donate electron charge into the surface. The adsorption energy follows the overlap population between the nitrogen and gold atoms.

Molecule	Mulliken Charge					Mulliken Population
	Gas Phase		Adsorbed Ontop			Au-N Overlap
	NH ₂	Substituent	NH ₂	Substituent	Substrate	
NH ₂ C ₆ H ₅	+0.002	-0.002	+0.106	-0.080	-0.022	0.024
NH ₂ C ₁₀ H ₇	+0.098	-0.098	+0.118	-0.065	-0.053	0.025
NH ₂ C ₁₄ H ₉	+0.106	-0.106	+0.112	-0.028	-0.084	0.027
NH ₃	+0.12	-0.12	+0.212	-0.128	-0.084	0.047
NH ₂ CH ₃	-0.018	+0.018	+0.046	+0.002	-0.048	0.054

Table 3: Mulliken population analysis, in units of the electron charge, showing the effects of substituents. Mulliken charges are given for the gas phase molecule separated into the sum of charges for the NH₂ component of the molecule and the substituents C₆H₅, C₁₀H₇, C₁₄H₉, H, CH₃ respectively. Corresponding Mulliken charges are given for the adsorbed molecule in the ontop site and total charge of the Au substrate. Overlap populations are for the adsorbed molecule.

3.2 Comparison with other binding groups

Here we compare the amine adsorption results with data for phosphine¹⁰, thiol^{20,25} and ethynylbenzene⁸ compounds. The interaction energies and geometries of these different classes of molecules on the Au(111) surface were obtained previously with the same computational method and therefore provide a meaningful comparison of the interaction strengths. Adsorption energies are more difficult to calculate in these cases because bond-dissociation occurs during adsorption.

Molecule	Binding Site	Height (Å)	E_1 (eV)	Reference
NH ₃	ontop	2.45	-0.24	This work
NH ₂ C ₆ H ₅	ontop	2.65	-0.13	This work
NH ₂ C ₁₀ H ₇	ontop	2.76	-0.13	This work
NH ₂ C ₁₄ H ₉	ontop	2.64	-0.20	This work
NH ₂ CH ₃	ontop	2.46	-0.32	This work
NH(CH ₃) ₂	ontop	2.55	-0.32	This work
NH(CH ₃) ₃	ontop	2.72	-0.25	This work
PH ₃	fcc	-	-	Ref. ¹⁰
PH ₂ CH ₃	fcc	-	-	Ref. ¹⁰
PH(CH ₃) ₂	ontop	2.74	-0.59	Ref. ¹⁰
P(CH ₃) ₃	ontop	2.53	-0.89	Ref. ¹⁰
SCH ₃	bridge, toward fcc	2.00	-1.85	Ref. ²⁰
SC ₆ H ₅	bridge	2.09	-1.43	Ref. ²⁰
SCH ₂ C ₆ H ₄ CH ₂ SH	bridge, towards fcc	2.10	-1.30	Ref. ^{25*}
HSCH ₂ C ₆ H ₄ CH ₂ SH	ontop	2.80	-0.17	Ref. ^{25*}
C≡CC ₆ H ₅	fcc	1.32	-2.99	Ref. ⁸

*Adsorption calculations were performed in this reference, however interaction energies were not given and are reported here for the first time.

Table 4: Interaction energies and heights of several amines, phosphines, thiols and ethynylbenzene on the Au(111) surface.

Table 4 lists the optimal binding site for each molecule, the ontop interaction energies and heights for the amine compounds are provided for comparison. It should be noted that the latter are interaction energies which do not include molecule or surface distortion energies upon adsorption and thus are different to the energies presented in Table 1.

The amine and phosphine compounds show similar overall bonding characteristics, the bond strengths in both cases are relatively weak, compared with thiolates or ethynylbenzene, and both sets of molecules prefer the low coordination site. Binding energies for dimethyl- and trimethylphosphine are stronger than the corresponding amines, however phosphine and methylphosphine are unbound. The same systematic increase in binding is not observed with increasing methyl substitution for the amine compounds. For the phosphine calculations bonding was shown to be predominantly through donation of electron density from the phosphorus atom into the gold surface, presumably from the lone pair, and a back donation of electron density from the gold into the P-C bond.¹⁰ This mechanism provides a possible explanation for the stronger bonding of the dimethylphosphine and trimethylphosphine compared with the corresponding amines: nitrogen is considerably more electronegative than phosphorus and hence donation of electron density into the gold surface is less for the amines thereby providing less stabilization of the gold-amine bond. A weak donation, back-donation mechanism is apparent in the Mulliken analysis of ammonia adsorption. The nitrogen atom donates 0.112e of charge into the Au surface from the 2s and 2p orbitals (on the ontop site) and 0.03e of charge is donated back to the hydrogen atoms. The net charge of $-0.082e$ on the Au atoms is distributed across the substrate. As well as any bond stabilization that occurs due to this donation / back-donation the substrate and adsorbate are also oppositely charged, as evidenced by the Mulliken charges, and there is a coulomb interaction between them. The Mulliken overlap populations between P and Au atoms in the ontop site are 0.15 and 0.21 for dimethyl- and trimethylphosphine respectively, the overlap for methylamine is 0.054 by contrast. There is considerably less covalent character to the amine-gold bond compared with the phosphine gold-bond.

The strongest interaction with the gold surface is observed for the ethynylbenzene radical in the fcc hollow site. The binding of methanethiol, benzenethiol and benzenedimethanethiol radicals with the gold surface is about half as strong. When the hydrogen atom is retained on the terminating sulfur of these thiol molecules, the adsorption with the surface is much weaker at -0.16 eV and is close to the ontop site. Both ethynylbenzene and the thiol molecules (where the terminal hydrogen is removed) can bind strongly to more than one site on the Au(111) surface, such as the two hollow sites and the bridge site. For ethynylbenzene, methanthiolate and benzenethiolate the binding energy only varies by about 0.1 eV between the two hollow sites and bridge site; the bridge is actually a saddle between the two hollow sites

for the ethynylbenzene.^{8,20} The ontop sites are also saddle points in the potential energy and are 0.3 and 0.5 eV less stable than the hollow or bridge sites for ethynylbenzene and the thiolates respectively.

The charge transfer upon adsorption of the ethynylbenzene radical is 0.1 electrons from the surface, the overlap population between the bonding carbon atom on the radical and each of the bonding Au atoms on the surface is around 0.12. Similar magnitudes are found for the charge and overlap populations for both methanethiolate and benzenethiolate. The bond to the surface for these molecules is considerably more covalent than either the amines or phosphines.^{8,20} Thus, for the group of molecules studied here, the trend in binding energies for the various anchoring atoms is $N < P < S < C$.

4. Conclusions

The adsorption of amine compounds on the Au(111) surface was studied using Density Functional Theory. The amines studied adsorb more strongly when coordinated to a gold adatom located in the fcc position on the (111) surface. Adsorption with the nitrogen atom in the ontop site is also possible, but this cannot be resolved within the accuracy of the theory. In higher coordinated sites, the adsorption energy is too low to suggest that the molecule can adsorb in these positions. Substitution of a hydrogen atom with methyl, phenyl, naphthyl, or anthracenyl groups does not significantly improve binding in this situation.

There is no systematic improvement in binding with increased substitution with methyl groups, as previously noted for phosphine adsorption on Au(111). A Mulliken population analysis indicates that a donation / back donation mechanism is at least partly responsible for the gold-amine bond, where the nitrogen atom donates charge into the surface which then back-donates into the amine molecule. A similar situation was found for phosphine molecules, although the bond is stronger because of the more considerable charge transfer. Nitrogen is more electronegative than phosphorous and hence may inhibit charge donation giving a weaker bond. Substituting phenyl rings onto the amine weakens the bond, again possibly because of further inhibition of electron donation; the phenyl substituents are more electron withdrawing relative to the methyl substituents. In all cases the adsorbate has a net positive charge and substrate a net negative charge, the overlap populations between nitrogen atom and bonding-gold atom are not large, but are not zero. There is some covalent and charge transfer character to the bond.

The data for amine compounds confirm a weak adsorption, with significant binding only in an under-coordinated adatom site. This may explain the reduced stochastic switching in molecular conductance experiments observed by various experimental groups. The amine molecules are only substantively bound to adatoms on the gold surface and not to other sites. Hence in molecular conductance experiments one might expect the I-V characteristic is dominated by molecules bound to adatoms only. Since molecular conductance is strongly influenced by the interface, i.e. bond, between molecule and electrode, for amines the observed conductance does not vary greatly. By contrast, for other molecules such as thiols a number of sites have very similar binding energies and molecular conductance experiments will show considerable variation depending upon which particular site is being probed.

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