

# Adsorption of ammonia on the gold (111) surface

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(Received 4 September 2001; accepted 26 February 2002)

We have modeled the adsorption of ammonia on the Au(111) surface at coverages of 1/4 and 1/9 of a monolayer using density-functional theory employing the pseudopotential method, periodic imaging, a plane-wave basis set, and the PW91 density functional. The geometries of the adsorbate and the surface are fully optimized. The adsorption is found to be highly favored on top of a surface atom. Adsorption energies of 26 and 32 kJ mol<sup>-1</sup> are obtained for the 1/4 and 1/9 of a monolayer coverage, respectively, extrapolating to 34 kJ mol<sup>-1</sup> at zero coverage; the experimental estimate is 32–42 kJ mol<sup>-1</sup>. Small changes in the work function are predicted and interpreted as arising from a surface layer whose effective dipole moment is 2.15 D, 0.77 D larger than the calculated value of isolated ammonia. Examination of the calculated charge density and the local electric field strengths indicate that the change in dipole moment is due to polarization effects and that ammonia to gold charge transfer is minimal, at most 0.01 *e* in magnitude. Qualitatively, the local densities of states and the charge distribution provide little indication of covalent bonding between the gold and ammonia, and quantitatively the adsorption is interpreted as arising from dispersive interactions with some contribution from polarization. This picture is in contrast with common notions of gold to ammonia binding which depict weak chemisorption rather than physisorption, but the usefulness of PW91 in distinguishing between these processes is questioned through examination of the calculated potential energy surface of Ne<sub>2</sub>. PW91 is shown only to mimic dispersive interactions using modified covalent terms. © 2002 American Institute of Physics. [DOI: 10.1063/1.1471245]

## I. INTRODUCTION

In order to interpret the nature of gas–surface interactions, knowledge of forces which govern the bonding mechanism at the interface between gaseous and solid phases is required. Systems of this type are very important. Heterogeneous catalysis and gaseous corrosion, for example, are reactive processes with enormous importance, while aerodynamic friction is an example of an important nonreactive process. Recent progress in theoretical methods and increasing computer power have provided the opportunity to obtain microscopic insight into such processes.

We report the first calculation from first principles of the adsorption of ammonia on a gold surface and interpret the results in terms of chemical bonding models; this uses density-functional theory and the PW91 density functional.<sup>1</sup> The adsorption and reaction of ammonia on transition metal surfaces has been studied extensively owing to its importance as a reactant or product in the field of catalysis (for early reviews, see Refs. 2 and 3). Experimental studies of ammonia adsorbed on a gold substrate, however, are rather sparse.<sup>4–7</sup> Theoretical studies of the interaction of ammonia with surfaces, aiming to shed light on the nature of the bonding, have been carried out for several late *d*-band metal substrates,<sup>8–15</sup> but not for gold. Most of the studies employed

atomic clusters as models for the metal substrate. These calculations have all found the atop-site binding preferred, with ammonia attached to the metal surface via its nitrogen atom. An early study<sup>10</sup> anticipated such a scenario for the adsorption of ammonia on most metals.

Chemically, the bonding between ammonia and a gold (111) surface could arise from a combination of a variety of effects including covalent bonding (via electron sharing involving the ammonia lone-pair orbital and the partially filled gold *s* band), electron transfer (via ligand to metal or even metal to ligand charge transfer), electrostatic effects such as charge polarization of the ammonia and/or the metal, and dispersive interactions. Often the term “weak chemisorption” is used<sup>4–7</sup> to describe the interaction between ammonia and gold, suggesting that weak covalent or electron-transfer effects are most significant. However, as dispersion may also be a significant contributor, and as density functionals of the type of PW91 typically perform poorly for this type of interaction,<sup>16</sup> at best treating it implicitly via modified covalent terms, we also examine in detail the interaction predicted by PW91 for Ne<sub>2</sub>.

## II. METHODOLOGY

The computations were done using the Vienna *ab initio* simulation package (VASP).<sup>17,18</sup> VASP utilizes an iterative

scheme to solve self-consistently the Kohn–Sham equations of density functional theory using residuum-minimization techniques and an optimized charge-density mixing routine. A plane-wave basis set is employed to expand the electronic wave functions, which facilitates the evaluation of the Hellmann–Feynman forces acting on atoms. Electron–ion interactions are accounted for through the use of ultrasoft pseudopotentials,<sup>19,20</sup> which allows the use of a low energy cutoff for the plane-wave basis set. For electron–electron exchange and correlation interactions the functional of Perdew and Wang (PW91),<sup>1</sup> a form of the generalized gradient approximation (GGA), is used in the current work. The relaxation of atom positions is performed via the action of a conjugate gradient optimization procedure.

The gold surface was modeled by supercells consisting of several atomic layers and vacuum. The application of periodic boundary conditions in all three Cartesian directions yields an infinite array of periodically repeated slabs separated by regions of vacuum. Two supercell geometries, with four and nine atoms per layer, respectively, were employed in order to simulate a high,  $\Theta = 1/4$  of a monolayer (ML), and low,  $\Theta = 1/9$  ML, coverage limit of adsorbed ammonia, the unit cell of which correspond to a  $(2 \times 2)$  and  $(3 \times 3)$  lateral geometry. In the case of ammonia adsorption on Pt(111) surface, saturation at  $1/4$  ML has been established.<sup>21</sup> Given the overall resemblance between thermal desorption spectra of ammonia on Au(111) (Ref. 6) and Pt(111),<sup>21</sup> and the strong dipole–dipole repulsion between adjacent parallel aligned ammonia molecules, higher coverage limits have been omitted from consideration. Lower limits, on the other hand, would involve larger supercells resulting in higher computational demands.

The lattice constant of gold was obtained from bulk computations of total energy versus the size of the unit cell. While this property is required as an input parameter to the subsequent surface-structure computations, calculations of this type are also useful as they provide an indication of the accuracy of the computational approach. An energy cutoff of 180 eV was used for the plane-wave expansion. The Brillouin zone integration was performed on a Monkhorst–Pack  $11 \times 11 \times 11$   $k$ -point mesh with a Methfessel–Paxton<sup>22</sup> smearing of 0.2 eV. The fit to an equation of state gives a lattice constant of 4.2 Å and a bulk modulus of 150 GPa. In order to evaluate the cohesive energy of gold, a single atom in a cubic cell with 12 Å large sides was used to approximate an isolated gold atom. Its total energy was then calculated using only the  $\Gamma$ -point in the Brillouin zone integration. A cohesive energy of 3.24 eV is obtained as the energy difference of a gold atom in bulk and the “isolated” atom. These values are in an acceptable agreement with those from experiments—4.08 Å, 170 GPa, and 3.81 eV, for the lattice parameter, bulk modulus, and cohesive energy, respectively.<sup>23</sup> A subsequent increase in the energy cutoff by 30% showed no significant change, indicating that the lower cutoff is appropriate.

For calculations involving ammonia, Brillouin-zone integrations have been done using  $5 \times 5 \times 1$  and  $3 \times 3 \times 1$  Monkhorst–Pack grids, respectively, with a Methfessel–Paxton smearing of 0.2 eV. An energy of 350 eV is used, as required by the pseudopotential of nitrogen.

TABLE I. Adsorption energies for NH<sub>3</sub> on the Au(111) surface, given in kJ mol<sup>-1</sup>.

$\Theta$ (ML)	Thickness	Top <sup>a</sup>	Flip	Bridge	fcc	hcp
1/4	6	25		5	4	1
1/4	4	26				
1/9	4	32	9			
0		34 <sup>b</sup>				

<sup>a</sup>Site average, standard deviation 2 kJ mol<sup>-1</sup>.

<sup>b</sup>Extrapolated, see text.

The  $(2 \times 2)$  supercell was used in conjunction with either four or six layers of gold atoms, while the  $(3 \times 3)$  supercells was only used with four layers. In each case, the layers of metal were separated by a region of vacuum of six atom layer equivalent thickness. The interlayer spacing is taken from the previously determined value of the bulk lattice parameter. For ammonia adsorption, two molecules, one each side of the slab, with an inversion center, have been employed to reduce the dipole–dipole interactions between neighboring cells. Unless otherwise specified, all calculations were for the configuration in which the nitrogen of ammonia faced the surface; alternate hydrogen-facing configurations are labeled “flipped.” The top and bottom layers were allowed to relax in each calculation, with inner layers frozen in the bulk positions.

### III. RESULTS

The energy of ammonia in the gas phase has been estimated using two molecules with an inversion center in a cell of the same size as the  $(3 \times 3)$  supercell. For this, the optimized N–H bond length and H–N–H bond angle are 1.02 Å and 105.7°, respectively, in good agreement with the experimental values of 1.012 Å and 106.7°.<sup>24</sup>

For the clean gold surface a calculation using the  $(2 \times 2)$  supercell shows very little relaxation for the top and bottom layer of the slab, in accord with the experimental result<sup>25</sup> for a clean Au(111) surface. The work function from the same calculation is found to be 5.23 eV, in excellent agreement with the experimental value of 5.26 eV.<sup>26</sup>

Ammonia adsorption was initially considered for nitrogen-facing configurations in which the nitrogen can be classified as lying on top, bridge, or hcp and fcc threefold hollow sites, and the corresponding adsorption energies on the  $(2 \times 2)$  6-layer supercell are listed in Table I. Apart from the atop adsorption, all sites result in very weak or almost no binding. Hence, only the atop case has been considered for use with the  $(3 \times 3)$  cell. Also, this configuration has been used to examine the dependence of the binding energy on the thickness of the gold slab and on the relative location of the two ammonia molecules with respect to each other, with the results again given in Table I. The values entered in this table for the top configuration are in fact the adsorption energies averaged over all possible locations, and the standard deviations in the energy is 2 kJ mol<sup>-1</sup> in each case. Variations of up to 7 kJ mol<sup>-1</sup> were found between individual structures, however. For the  $(2 \times 2)$  supercell, varying the thickness

TABLE II. Geometries for  $\text{NH}_3$  adsorbed atop. Distances between atoms, N–Au and N–H, as well as the top layer buckling  $d_{11}^{\text{Au–Au}}$ , are given in Å.

$\Theta$ (ML)	N–Au	N–H	$\angle\text{H–N–H}$	$\angle\text{H–N–Au–H}$	$d_{11}^{\text{Au–Au}}$
1/4	2.58	1.02	$110.2^\circ$	$120.0^\circ$	0.11
1/9	2.45	1.02	$109.7^\circ$	$119.9^\circ$	0.04

from four to six layers resulted in only the relatively small change of  $1 \text{ kJ mol}^{-1}$  and hence only four layers were used with the  $(3 \times 3)$  supercell.

The major contribution to the change in adsorption energy as a function of coverage is the change in the dipole–dipole interactions between neighboring ammonia molecules, an interaction which decreases with the third power of the length of the unit cell. This result may be used to extrapolate<sup>7</sup> our calculated adsorption energies to zero coverage, and we obtain  $34 \text{ kJ mol}^{-1}$ . A similar correction is also obtained by considering the expansion of the unit cell containing just a single ammonia molecule, corrected for the change in dipole moment discussed below. This suggests that there are no strong chemical interactions between neighboring ammonia molecules on the  $(2 \times 2)$  cell, although interactions of the order of those found between the ammonia molecules on different sides of the metal are naively expected.

The corresponding optimized geometries for the atop binding are given in Table II. In both cases ammonia is found to adsorb with its threefold axis perpendicular to the surface, coordinated via the nitrogen atom. The molecule is free to rotate around the axis, as the energy differences between various azimuth orientations are less than the accuracy of the present computations. The presence of ammonia induces some buckling in the top layer of the gold surface, shown in Table II as  $d_{11}^{\text{Au–Au}}$ . It concerns only the Au atoms bound to N, and is significant only in the higher coverage case for which  $d_{11}^{\text{Au–Au}} = 0.11 \text{ Å}$ . Relaxations in the lateral directions did not occur.

An interesting phenomenon often observed on surfaces is the adsorption-induced change in the work function. It originates from surface dipoles and charge transfer between adsorbate and substrate and is obtained as the difference between the electrostatic potential in the middle of the vacuum region and the Fermi energy. The extent of the vacuum region must be sufficient to ensure that the electrostatic potential has a uniform value at all points on its central plane. Its length must increase with decreasing coverage and we use nine atomic layers equivalent thickness at 1/4 ML and eleven at 1/9 ML. The results indicate a decrease in the work function of Au(111) induced by ammonia adsorption of 1.15 and 1.90 eV for the ammonia coverages of 1/9 and 1/4 ML, respectively. While the sign of the change as well as its increase with coverage are typical for ammonia on transition metal surfaces, the magnitude of the change for the Au(111) surface is somewhat lower than for most others. In the case of Rh(111), for example, it amounts to  $-2.5 \text{ eV}$  at the higher coverage<sup>15</sup> and for Pt(111) the magnitude at saturation coverage is  $-3.0 \text{ eV}$ , one of the largest work function changes ever reported.<sup>21</sup> Using the Helmholtz equation,<sup>27</sup> which gives

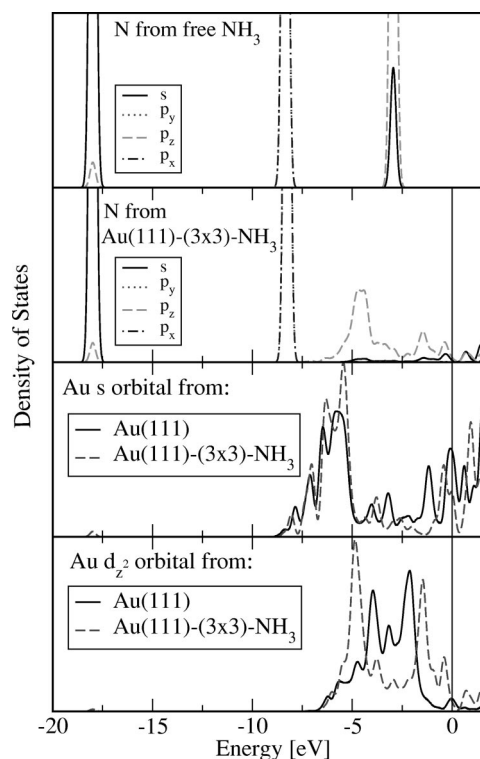


FIG. 1. Projected densities of states for the nitrogen  $s$  and  $p$  orbitals as well as the  $s$  and  $d_{z_2}$  orbitals of the bound gold atom as a function of energy relative to the Fermi level.

a linear relationship between the change in the work function and the adsorbate-induced dipole on the surface, an effective dipole moment of 2.15 D per molecule is obtained for the 1/9 ML coverage of ammonia on Au(111). This is significantly enhanced from the value of 1.47 D observed for free ammonia. For the adsorption on Rh(111) and Pt(111) values of 1.9 D and 2.0 D, respectively,<sup>15,21</sup> were obtained in the same manner in the high-coverage (i.e., nonlinear) limit.

In order to obtain insight into the electronic factors that control the adsorption, projected densities of states (PCDOS) have been calculated by projecting the wave function onto atom-centered spherical harmonic basis functions, considering only the electron density found within nonoverlapping spheres centered on each atom. The PCDOS for orbitals which show detectable change on binding are shown in Fig. 1, where they are compared to their unbound values. These orbitals are the nitrogen  $s$  and  $p$  orbitals as well as the  $s$  and  $d_{z_2}$  orbitals on the bonded gold atom. Clearly, a strong interaction occurs between the  $p_z$ -dominated nitrogen lone-pair orbital and the gold  $d_{z_2}$  orbital, but as both orbitals are doubly occupied no net covalent or charge-transfer interaction can occur and hence the interaction contributes only weakly to chemical bonding. Covalent bonding can occur only through interactions of the unfilled gold  $s$  band and the lone pair, but as Fig. 1 shows, only inconsequential interactions of this type are evident. Spin–orbit coupling mixes  $d \rightarrow p$  excitation with the ground state<sup>28</sup> and hence permits significant covalent interactions to occur with the partially vacated  $d_{z_2}$  orbital. As this effect is not included in these calculations, an underestimation of the ammonia–gold bond strength by

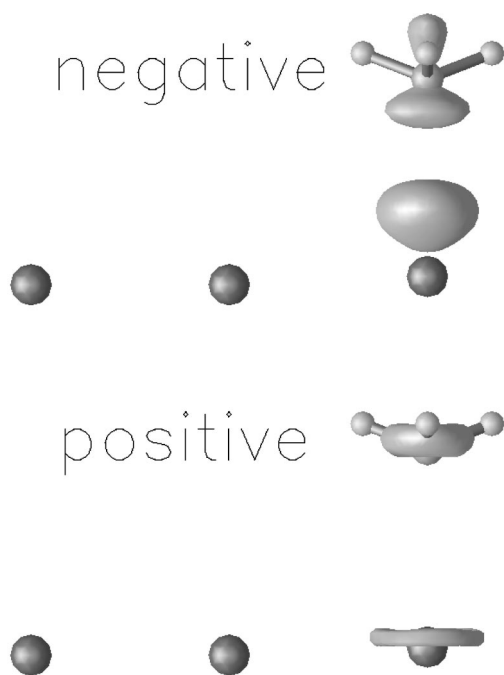


FIG. 2. Isosurfaces of differential charge of Au(111)-H<sub>3</sub>(2×2). Upper panel: negative value indicating electron deficit (an isovalue of 0.022 e/Å<sup>3</sup>). Lower panel: positive value indicating electron surplus (an isovalue of 0.017 e/Å<sup>3</sup>).

~20% is anticipated. Neglecting spin-orbit coupling, covalent bonding interactions are expected to be of minor importance, however.

As there is no evidence of any net electron transfer involving any orbital, polarization appears to be the only significant effect on the electronic structure of both the metal and ligand arising due to the adsorption of ammonia on the—chemically inert—Au(111) surface. The charge redistribution leads to local dipole moments on the surface which contribute to the change in the work function, as previously quantified. Further insight into the nature of this interaction can be obtained from the differential charge density, i.e., the charge density of the whole system from which the densities of the adsorbate and the substrate have been subtracted. The latter are to be evaluated for the distorted atom geometries taken from the calculation of the adsorbate-substrate complex, rather than for relaxed geometries, in order to visualize charge flow as arising from the adsorption. The isosurfaces of the differential charge are displayed in Fig. 2. Two observations can be made. First, the change in density is very low in magnitude. All the isosurfaces that extend over an appreciable space region have very small values. Second, the charge difference is spatially confined to the admolecule and the underlying atom indicating qualitatively that the major effect is internal charge redistribution, i.e., polarization of the two subsystems, rather than say adsorbate to metal charge transfer. No charge buildup was found in the region between the gold and nitrogen atoms indicating again that covalent bonding effects are not paramount.

#### IV. INTERPRETATION AND CONCLUSIONS

It is worthwhile to compare the polarization effects implied by Fig. 2 with the effective surface dipole evaluated from the Helmholtz equation. Quantitatively, the polarization can be estimated from values of the electric field strengths emanating from the ammonia and the surface and the polarizabilities of ammonia and the attached gold atom. The electric field of a free ammonia molecule (in its adsorbed configuration) at the position of the bound gold atom is 0.0128 au, while that emanating from the surface at the separation of the nitrogen atom is -0.0097 au. We computed the polarizability of a gold atom using GAUSSIAN 98 (Ref. 29) with the PW91 functional and the LANL2DZ basis,<sup>30</sup> obtaining 37 a.u. in agreement with previous higher-level calculations of 39 a.u.,<sup>31</sup> for ammonia, the polarizability similarly calculated using the PW91 functional and the aug-cc-pVDZ basis<sup>32</sup> is 16.5 a.u. (15.0 a.u. isotropic), close to the observed value of 18.9 a.u.<sup>24</sup> From these values, the estimated induced dipole at the ammonia is -0.4 D while that at the connected gold atom is 1.2 D; adding these to the calculated dipole moment of the ammoniac monomer of 1.5 D predicts a total surface dipole of 2.3 D, in good agreement with the value of 2.15 D deduced using the Helmholtz equation. These induced moments correctly reflect the density distributions shown in Fig. 2; the charge flow from nitrogen upwards tends to reduce the ammonia dipole, while the downwards flow on the gold atom would result in a dipole moment with the same orientation as that for the molecule. While this calculation ignores the effects of quadrupole and higher moments, polarization of neighboring gold atoms, and does not include a self-consistent description of the field strengths, it clearly indicates that charge-transfer contributions are not required in order to understand the calculated changes in the work function due to ammonia binding. A net charge transfer of just 0.05 *e* from nitrogen to its attached gold atom would be sufficient to account for the 0.65 D change in effective dipole moment, and so it appears that the actual amount of net charge transfer is less than 0.01 *e*.

From the above field strengths and induced dipole moments, the contribution of the polarization terms to the binding energy can be estimated. This amounts to 8.0 kJ mol<sup>-1</sup> for gold polarization and 2.0 kJ mol<sup>-1</sup> for ammonia polarization or 10 kJ mol<sup>-1</sup> total. An alternate estimate of the polarization energy of the gold substrate can be obtained from the image charge approximation for a continuous metallic surface assumed to pass through the nuclei of the surface atoms; this predicts 5.1 kJ mol<sup>-1</sup>, in reasonable agreement with the previous atom-based estimate of 8.0 kJ mol<sup>-1</sup>. Using either value, the total polarization energy is much less than the estimated zero-coverage binding energy of 34 kJ mol<sup>-1</sup>. Polarization is known to be the dominant term responsible for physisorption of molecules onto *sp* metal surfaces such as those of aluminum,<sup>33</sup> but appears inadequate for ammonia interacting with gold. As we have argued that covalent and charge-transfer effects are minimal, the remaining source of the binding energy must be electron-correlation effects such as dispersion, an effect expected to be much stronger for interactions with gold than with aluminum.

The longest-range component of the dispersive energy is

the London term whose isotropic component is crudely estimated as<sup>34</sup>

$$V_{\text{disp}} = -\frac{3}{2} \frac{I_{\text{NH}_3} I_{\text{Au}}}{I_{\text{NH}_3} + I_{\text{Au}}} \frac{\alpha_{\text{NH}_3} \alpha_{\text{Au}}}{R^6}, \quad (1)$$

where  $R$  is the Au–N separation,  $I$  are ionization energies, and  $\alpha$  are isotropic polarizabilities. At the equilibrium geometry this term contributes 37 kJ mol<sup>-1</sup> to the binding energy. It is thus quite plausible that this term, plus contributions from higher-order dispersive interactions, constitute the majority of the attractive terms leading to bonding; the energy at the equilibrium geometry would thus arise primarily from the competition between these terms and the exponentially-decaying exchange repulsion terms. In addition to the London term, significant contributions from higher-order orientationally dependent dispersive interactions<sup>35</sup> are expected due to the previously demonstrated strong interaction between the filled gold  $d_{z^2}$  and nitrogen lone-pair orbitals.

Dispersion is a long-range correlation that is poorly represented by currently available density-functionals. Our previous qualitative arguments suggest that in reality the gold–ammonia interaction is primarily dispersive in nature, but it is questionable as to whether or not PW91 leads to the same conclusion. A good quantitative check is to examine the long-range form of the interaction and check for the  $R^{-6}$  dependence typical of a dispersive interaction. However, as alternative contributions to the ammonia–surface interaction such as polarization scale as  $R^{-5}$ , proper discrimination could not be achieved. However, the basic problem can be examined by consideration of the binding in noble-gas dimers.<sup>16</sup> All density-functionals so far considered<sup>16</sup> produce potential energy surfaces of either very poor shape and/or orders of magnitude under or over estimations of the well depth. This suggests that, if the major attractive forces for ammonia on gold are dispersive in nature, then the quality of the computational results will be highly influenced by the nature of the density functional used. We chose PW91 as it has been argued<sup>36</sup> that, unlike most density functionals, it provides a reasonable description of van der Waals interactions between molecules such as O<sub>2</sub>, N<sub>2</sub>, and CO. The performance of PW91 for modeling the purely dispersive interactions between noble-gas atoms has not previously been considered, however. We show in Fig. 3 the potential energy surface for Ne<sub>2</sub> evaluated using PW91 and that obtained experimentally,<sup>37</sup> a surface which is known as “HFD-B.” Both surfaces are fitted by the universal<sup>38</sup> covalent potential

$$V_{\text{cov}} = -E_0(1+a)e^{-a}, \quad a = \alpha(R-R_m), \quad (2)$$

and the basic van der Waals exp-6 potential of Buckingham,<sup>35</sup>

$$V_{\text{vdW}} = Ae^{-\alpha R} - BR^{-6}, \quad (3)$$

which can be improved if necessary.<sup>38,39</sup> It is clear from the figure that the van der Waals potential fits the experimental data while the covalent potential fits the PW91 results. The PW91 well depth is also four times too deep; while this result appears poor, it is actually much better than that obtained for other common density functionals,<sup>16</sup> and PW91 is

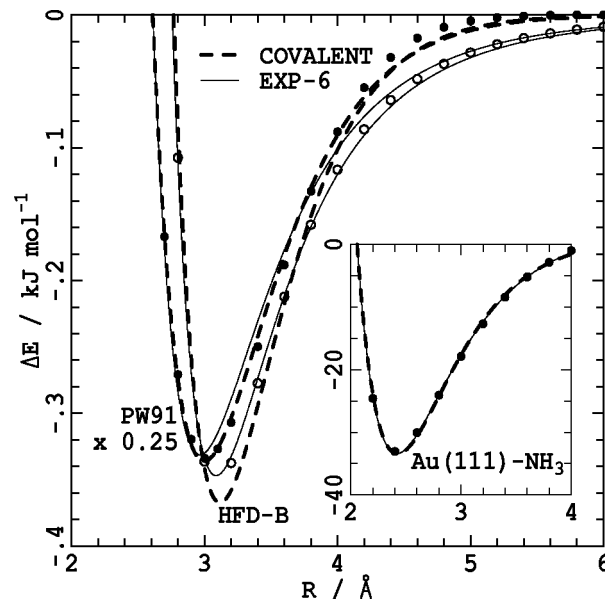


FIG. 3. The potential energy of Ne<sub>2</sub> from the experimental HFD-B surface (Ref. 37) (open circles) and from PW91 (filled circles), fitted using the covalent and van der Waals (exp-6) functions. The insert shows the PW91 energy of one atop configuration of the ammonia bound to the (3×3) cell of gold (111) as a function of extension of the gold to nitrogen separation  $R$  and its essentially equivalent fits to the two functional forms.

in fact the only functional known to reproduce the equilibrium bond length and the shape of the well region at all satisfactorily. Our conclusion is that, while PW91 has been shown<sup>36</sup> to reproduce properties of some van der Waals systems, it does so empirically using covalent terms to mimic van der Waals ones and so is not expected to be generally reliable. The Au(111)–NH<sub>3</sub> potential is shown in the insert of Fig. 3 for one conformation of the ammonia pair on the (3×3) gold surface. The energy profile can equally be fitted by the covalent and van der Waals formulas indicating that this empirical process is indeed pertinent to the PW91 treatment of the gold–ammonia interaction.

To further evaluate the strengths and weaknesses of our computational approach, we have examined in detail<sup>28</sup> the bonding in the AuNH<sub>3</sub> complex using PW91 with and without the use of ultrasoft pseudopotentials, and with and without spin–orbit coupling corrections, as well as with extensive coupled-cluster CCSD(T) (Ref. 40) calculations. The results indicate that PW91 overestimates binding energies by 15% compared to CCSD(T), that spin–orbit coupling produces an equal but opposite effect, and that use of the ultrasoft pseudopotentials causes the binding to be underestimated by 25%. The increased binding due to spin–orbit coupling occurs as  $d \rightarrow p$  excited states of gold which covalently bond to ammonia are mixed into the ground state. This effect may be specific to heavy metals such as gold and appears unnecessary to explain the binding in silver–ammonia and silver–water complexes.<sup>41</sup> Ultrasoft pseudopotentials have been shown to produce excellent molecular geometries, both in general<sup>42</sup> and for gold–ammonia clusters,<sup>28</sup> but to our knowledge there has been no systematic studies of their effects on binding energies. It is likely that the effects are more severe for light, electron dense atoms such as nitrogen, and

may be overcome using the recently developed projector augmented-wave (PAW) method.<sup>42</sup> In summary, the VASP ultrasoft-pseudopotential PW91 binding energy for the complex was found to be only 75% of the best-estimate value. Here, this method predicted an ammonia to Au(111) adsorption energy of 34 kJ mol<sup>-1</sup> (see Table I). Based on the analogy to the cluster calculation, we would anticipate the adsorption energy to be underestimated by ~10 kJ mol<sup>-1</sup>. Experimentally, the well depth at zero coverage has been estimated from thermal desorption spectra<sup>6,7</sup> as 32–42 kJ mol<sup>-1</sup> and so the calculated and experimental data are in reasonable agreement.

The cluster studies<sup>28</sup> also showed that, of all the density functionals considered including B3LYP,<sup>43</sup> only PW91 produced a potential-energy surface of reasonable shape, though the binding at large distances was significantly enhanced. Also, its binding energy at the equilibrium geometry was by far the closest to the best-estimate value. Hence PW91 was shown to be the optimal method available for studying ammonia bonded to Au(111).

Finally, we have also calculated the PW91 and CCSD(T) surfaces for a gold atom interacting with ammonia with the ammonia inverted in the “flipped” geometry with its hydrogens facing the gold atom. This potential surface has a minima near  $R = 2.85 \text{ \AA}$ . At this Au-N separation, the CCSD(T) energies for the nitrogen-facing and flipped isomers are 31 and 17 kJ mol<sup>-1</sup>, respectively, while the corresponding PW91 values are 39 and 31 kJ mol<sup>-1</sup>. Hence we see that the medium-range parts of the potential surfaces are not dominated by strong orientational effects usually associated with charge-transfer or covalent bonding, with PW91 in fact showing less chemical effects than CCSD(T). Further, neither isomer shows bonding at the Hartree–Fock level and hence it is clear that the major bonding arises from electron correlation effects such as dispersion.

The binding of the flipped structure to the surface is shown in Table I and is 9 kJ mol<sup>-1</sup>, much less than the PW91 value obtained for the AuNH<sub>3</sub> complex of 31 kJ mol<sup>-1</sup>, though the equilibrium bond length is only slightly larger. A major contribution to the difference is likely to be enhanced exchange repulsions between the hydrogens and the other gold atoms on the surface. Also, the binding energies for the bridge, fcc, and hcp sites shown in Table I are much lower than those for the top site. This could be interpreted as being due to a decrease in chemisorption due to unfavorable bonding interactions with the gold. Alternatively, it could be due to increased exchange repulsion forcing the bond lengths out to the calculated values of ~3.4 Å. At this bond length, the London dispersion terms would be an order of magnitude weaker than those for the top binding site and hence the rather weak bondings can be interpreted without the need to evoke strong chemical binding effects.

In conclusion, geometries and binding energies for ammonia adsorption on the Au(111) surface have been calculated for low and moderate coverages. Results of the present work compare reasonably with those arising from the theoretical calculations involving the interactions of NH<sub>3</sub> with other metal substrates. The adsorption energies and changes in the work function, while small, reproduce the available

experimental data. Only weak changes are observed in the calculated electronic properties of the system. While the term “weak chemisorption” is frequently used<sup>4–7</sup> to describe the interaction between ammonia and gold, at least for the chemically inert Au(111) surface no evidence that supports this point of view has been found. Rather, the bonding appears to be primarily dispersive in nature, with a quantifiable contribution arising also from charge polarization. PW91 is found to represent this dispersive interaction empirically but reasonably accurately.

## ACKNOWLEDGMENTS

The work was supported by the Australian Research Council. The use of supercomputer facilities at the Australian Partnership for Advanced Computing (APAC) is gratefully acknowledged.

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