

Chemisorption theory of ammonia on copper

Citation for published version (APA):

Biemolt, W., Kerkhof, van de, G. J. C. S., Davies, P. R., Jansen, A. P. J., & Santen, van, R. A. (1992). Chemisorption theory of ammonia on copper. *Chemical Physics Letters*, 188(5-6), 477-486.
[https://doi.org/10.1016/0009-2614\(92\)80852-3](https://doi.org/10.1016/0009-2614(92)80852-3)

DOI:

[10.1016/0009-2614\(92\)80852-3](https://doi.org/10.1016/0009-2614(92)80852-3)

Document status and date:

Published: 01/01/1992

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Chemisorption theory of ammonia on copper

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Received 18 April 1991; in final form 25 October 1991

We present local-density-approximation calculations of ammonia adsorption on copper clusters of different sizes (6 to 18 atoms) modelling the (100) and (111) surface. Including for some of the copper atoms only one instead of eleven electrons explicitly in the calculation, did not always work satisfactorily. Comparison of adsorption energies for clusters of related geometry indicates a preference for onefold adsorption. This is due to the Pauli repulsion of the lone-pair orbital of ammonia with the copper 3d electrons, which is minimal for onefold adsorption, as well as an interaction with 4s electrons, which is most attractive in the onefold geometry.

1. Introduction

The interaction of ammonia with copper surfaces is of considerable experimental as well as theoretical interest. From clear surfaces, condensed ammonia desorbs molecularly at approximately 200 K, which assuming a pre-exponential factor of 10^{13} s^{-1} corresponds to a heat of adsorption of approximately 50–60 kJ mol⁻¹. In the presence of preadsorbed oxygen, however, ammonia remains at the surface to above 240 K, and there is some activation of the nitrogen–hydrogen bond [1]. At room temperature, this interaction can lead to the rapid replacement of the oxygen by an adsorbed nitrogen-containing species. The study of the various copper clusters with ammonia presented here will serve as a reference to follow-up studies on ammonia dissociation in the presence and absence of an oxygen atom.

The local-density approximation (LDA) has proven to be a very useful tool in the study of the chemical bond between an adsorbate and a metal surface [2]. The metal surface in these kinds of studies is usually modelled by (small) clusters. One question to be answered is whether a procedure can be found to simulate chemisorption to surfaces by adsorption on clusters. This general question has also been addressed by several other authors [3]. We have

decided to look for trends in adsorption energies by comparing adsorption on various clusters of related geometries. As far as trends are concerned, representing a surface by a well-chosen cluster appears to be a very reasonable approximation. Slab calculations, where the surface is represented by infinite layers of atoms, would be a better approach when one is interested in quantitatively more accurate results [4].

Examining the copper–ammonia system shows that chemical bonding is mainly controlled by the interaction of the doubly occupied lone-pair orbital of ammonia, directed away from the molecule, towards the copper surface. Because the energy of the lowest unoccupied molecular orbitals is high, their interaction with the metal surface is expected to be less by more than an order of magnitude.

Earlier quantum-chemical studies [5] predicted that the interaction of the occupied copper d orbitals with the ammonia lone-pair orbital is onefold directing. The interaction with the lowest unoccupied ammonia orbitals, which have π symmetry, would prefer higher coordination sites, but is probably too weak. In the case of Ni(111)/CH₃, it was found that the interaction of the partially occupied nickel s and p orbitals with the CH₃ singly occupied valence orbital, which is capable of forming electron-pair bonds,

prefers higher coordination sites [6–8]. We expect for ammonia a competition between the interaction with the copper d orbitals, favouring onefold adsorption, and with the copper s and p orbitals, favouring high-coordinated adsorption. In contrast to this expectation, the results of our calculations showed that the interaction with the s-valence electrons also favours the onefold position.

The ab initio LDA method we used in our study enables us to separate the contributions to the adsorption energy into a repulsive part which derives from electrostatic interactions and exchange repulsion, resulting in a steric repulsion, and an attractive part that derives from orbital interaction [9]. We will analyze the changes in these two contributions for all the different clusters and adsorption geometries studied.

2. Method and cluster models

We performed non-relativistic, spin-restricted calculations using the local-density approximation with the Vosko–Wilk–Nusair (VWN) local-spin-density (LSD) potential [10] as implemented in the Amsterdam-density-functional (ADF) program suite by Baerends and co-workers [11]. In this set of programs, the molecular orbitals are represented as lin-

ear combinations of atomic Slater-type orbitals (STO). Integrals are computed numerically [12] and adsorption energies are computed with the Ziegler transition-state method [13].

For nitrogen, the 1s core is kept frozen, and for copper, the electrons up to and including the 3p core are kept frozen. In the “mixed cluster approach”, for some of the copper atoms the electrons up to and including the 3d core are kept frozen. Table 1 shows the exponents of the STO basis sets and table 2 the fitting functions we used in our calculations. Single- ζ functions are used for core orthogonalization. The valence functions are of double- ζ quality with a triple- ζ d for copper (when included as valence). For all the atoms, polarization functions have been added.

Fig. 1 shows all the clusters and adsorption geometries we studied. The clusters are labelled according to the number of atoms in each layer. An asterisk in this notation denotes that the core for the copper atoms in that layer has been kept frozen until the 4s electrons (only one valence electron per atom remains). For the other copper atoms, the core has been kept frozen up to and including the 3p electrons (leaving a total of eleven valence electrons per atom). The copper–copper distance is set equal to the nearest-neighbour distance in the bulk: 2.556 Å [14]. For ammonia, the free-gas geometry is used: the N–H bond distance is 1.008 Å, and the H–N–H bond an-

Table 1^{a)}
Exponential coefficients for the basis functions

| Cu | | | N | | | H | | | | | |
|----|-------|-------|----|-------|-------|----|------|---|----|------|---|
| 1S | 34.80 | c | 1S | 24.45 | v | 1S | 8.74 | c | 1S | 1.28 | v |
| 1S | 27.00 | c | 2S | 8.35 | v | 1S | 5.90 | c | 1S | 0.76 | v |
| 2S | 11.35 | c | 3S | 6.60 | v | 2S | 1.50 | c | 2P | 1.00 | v |
| 2S | 6.60 | c | 2P | 11.71 | v | 2S | 2.50 | c | | | |
| 3S | 6.70 | c | 3P | 4.53 | v | 2S | 5.15 | c | | | |
| 3S | 4.05 | c | 3D | 1.28 | v 3d+ | 1S | 6.38 | v | | | |
| 4S | 0.86 | c | 3D | 3.10 | v 3d+ | 2S | 1.46 | v | | | |
| 4S | 1.40 | c | 3D | 6.90 | v 3d+ | 2S | 2.38 | v | | | |
| 4S | 2.40 | c | 4S | 1.00 | v 3d+ | 2P | 1.12 | v | | | |
| 2P | 16.05 | c | 4S | 1.90 | v 3d+ | 2P | 2.58 | v | | | |
| 2P | 10.45 | c | 4P | 2.00 | v 3d+ | 3D | 2.00 | v | | | |
| 3P | 6.00 | c | 3D | 2.43 | 3 3d– | | | | | | |
| 3P | 3.50 | c | 4S | 1.00 | v 3d– | | | | | | |
| 3D | 1.28 | c 3d– | 4S | 1.90 | v 3d– | | | | | | |
| 3D | 3.10 | c 3d– | 4P | 1.00 | v 3d– | | | | | | |
| 3D | 6.90 | c 3d– | 4P | 1.90 | v 3d– | | | | | | |

^{a)} c=core and v=valence (3d+: only for unfrozen 3d orbitals, and 3d–: only for frozen 3d orbitals).

Table 2
Exponential coefficients for the fit functions

| Cu | N | | H | | | | |
|----|-------|----|-------|-------|--------|----|------|
| 1S | 48.90 | 2P | 36.16 | 1S | 12.760 | 1S | 2.56 |
| 2S | 47.17 | 3P | 22.22 | 2S | 13.878 | 1S | 2.04 |
| 3S | 41.80 | 4P | 13.98 | 2S | 9.192 | 1S | 1.52 |
| 3S | 27.12 | 5P | 9.02 | 3S | 7.507 | 3S | 2.00 |
| 4S | 23.39 | 6P | 5.94 | 3S | 4.518 | 2P | 2.28 |
| 4S | 15.98 | 6P | 3.38 | 3S | 2.719 | 2P | 1.76 |
| 5S | 13.65 | 3D | 31.35 | 3S | 1.637 | 3D | 2.00 |
| 5S | 9.67 | 4D | 17.50 | 2P | 8.760 | | |
| 6S | 8.23 | 5D | 10.14 | 3P | 6.636 | | |
| 6S | 6.00 | 6D | 6.06 | 3P | 3.725 | | |
| 6S | 4.37 | 6D | 3.14 | 3P | 2.091 | | |
| 7S | 3.72 | 4F | 18.61 | 3D | 8.380 | | |
| 7S | 2.77 | 5F | 10.78 | 3D | 4.402 | | |
| 7S | 2.06 | 5F | 5.26 | 3D | 2.312 | | |
| | | 5G | 13.80 | 4F | 4.580 | | |
| | | 5G | 4.38 | 4F | 2.068 | | |
| | | | 5G | 4.000 | | | |

gle is 107.3° [14]. A full geometry optimization of the Cu(1)-NH₃ system, when the N-H bond distance and the H-N-H bond angle are also optimized, lowers the calculated adsorption energy by only 0.1 eV. This is about the same size as the error in the calculation due to numerical inaccuracies, and therefore the geometry optimization of the ammonia is ignored in this discussion. The copper-nitrogen distance was optimized for each cluster. For the clusters with the optimum copper-nitrogen distance, we also included gradient or non-local corrections for the exchange [15] and correlation [16]. With these corrections, the calculated energies are in better agreement with the experimental value, but the differences between the various clusters essentially remain the same.

3. Results and discussion

The results of the calculations made on the ammonia adsorption on all the copper clusters (fig. 1) are shown in tables 3-5. Here, the adsorption energy is defined as

$$\Delta E_{\text{ads}} = E(\text{Cu}_n\text{-NH}_3) - E(\text{Cu}_n) - E(\text{NH}_3). \quad (1a)$$

This adsorption energy can be decomposed in two main contributions [9],

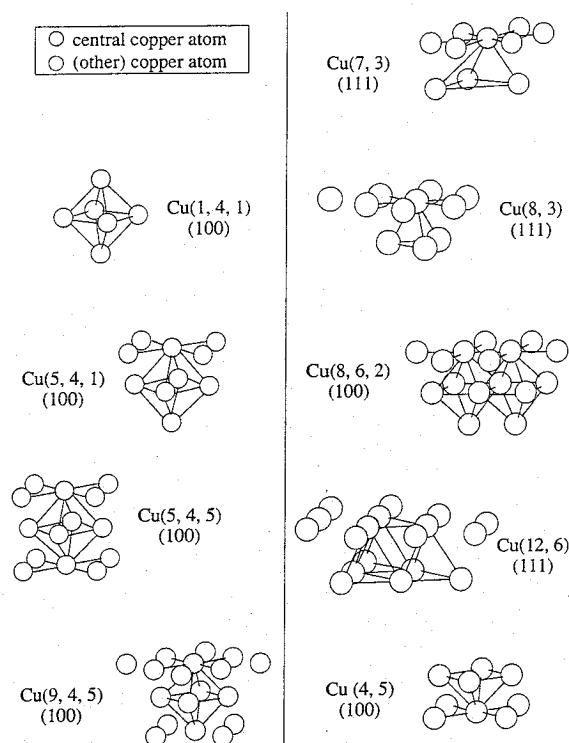


Fig. 1. The cluster geometries studied. The clusters are labelled according to the number of atoms in each layer, so Cu(*I, J, K*) refers to *I* copper atoms in the first layer, *J* in the second, and *K* in the third. The surface of the cluster models has also been indicated.

$$\Delta E_{\text{ads}} = \Delta E_{\text{steric}} + \Delta E_{\text{int}}, \quad (1b)$$

where ΔE_{steric} is the energy change due to superposition of Cu_{*n*} and NH₃ without changing their molecular orbitals. This can be considered to be the contribution due to steric repulsion. The orbital interaction energy, ΔE_{int} , is the energy change upon the subsequent formation of the molecular orbitals of Cu_{*n*}-NH₃. The separate contributions are presented in the same tables.

The effect of keeping the core frozen up to and including the 3d electrons was studied for the Cu(5, 4, 1) cluster. This approximation should result in a considerable reduction in the size of the calculations when the d-valence electrons on all atoms next to those directly in contact with adsorbate are frozen, in this case Cu(1+4*, 4*, 1*). Such kinds of calculations have given successful results earlier, espe-

Table 3

Energy breakdown (eV) For $\text{Cu}_{10}\text{-NH}_3$ used to study the influence of a copper 3d-frozen core. The copper-nitrogen distance is fixed at 2.03 Å

| Cluster geometry | Steric repulsion (eV) | Orbital interaction (eV) | Adsorption energy (eV) | CPU time (%) |
|------------------|-----------------------|--------------------------|------------------------|--------------|
| Cu(5, 4, 1) | 0.60 | -1.40 | -0.80 | 100 |
| Cu(5, 4, 1*) | 0.65 | -1.41 | -0.76 | 91 |
| Cu(5, 4*, 1) | 0.58 | -1.32 | -0.74 | 81 |
| Cu(1+4*, 4, 1) | 0.85 | -1.24 | -0.39 | 85 |
| Cu(5, 4*, 1*) | 0.61 | -1.33 | -0.72 | 75 |
| Cu(1+4*, 4*, 1*) | 0.85 | -1.18 | -0.33 | 63 |
| Cu(5*, 4*, 1*) | 2.60 | -1.17 | 1.42 | 60 |

Table 4

Geometry optimization, energy breakdown (eV), and vibration frequency for $\text{Cu}_{10}\text{-NH}_3$ used to study the influence of a copper 3d-frozen core

| Cluster geometry | Cu-N distance (Å) | Steric repulsion (eV) | Orbital interaction (eV) | Adsorption energy (eV) | ω (cm^{-1}) |
|------------------|-------------------|-----------------------|--------------------------|------------------------|-------------------------------|
| Cu(5, 4, 1) | 2.13 | 0.31 | -1.13 | -0.83 | 305 |
| Cu(5, 4, 1*) | 2.14 | 0.34 | -1.12 | -0.79 | 281 |
| Cu(5, 4*, 1) | 2.15 | 0.26 | -1.03 | -0.77 | 287 |
| Cu(1+4*, 4, 1) | 2.29 | 0.21 | -0.73 | -0.52 | 168 |
| Cu(5, 4*, 1*) | 2.15 | 0.28 | -1.03 | -0.76 | 284 |
| Cu(1+4*, 4*, 1*) | 2.33 | 0.15 | -0.64 | -0.48 | 174 |
| Cu(5*, 4*, 1*) | | | not bonding | | |

Table 5^{a)}

Geometry, energy breakdown (eV), and vibrational frequency for the studied $\text{Cu}_n\text{-NH}_3$ systems

| Cluster geometry | Surface | Cu-N (Å) | Steric repulsion | Orbital interaction | Adsorption energy | + Non-local corrections | ω (cm^{-1}) |
|------------------|-----------|----------|------------------|---------------------|-------------------|-------------------------|-------------------------------|
| Atom | | | | | | | |
| Cu(1) | - {0} | 2.03 | 1.32 | -2.20 | -0.88 | -0.41 | 335 |
| 1-fold | | | | | | | |
| Cu(1, 4, 1) | (100) {4} | 1.94 | 0.78 | -2.41 | -1.63 | -1.09 | 400 |
| Cu(5, 4, 1) | (100) {8} | 2.13 | 0.31 | -1.13 | -0.82 | -0.26 | 305 |
| Cu(5, 4, 5) | (100) {8} | 2.13 | 0.21 | -1.15 | -0.94 | -0.36 | 293 |
| Cu(9, 4, 5) | (100) {8} | 2.07 | 0.22 | -1.37 | -1.15 | -0.50 | 344 |
| Cu(7, 3) | (111) {9} | 2.15 | 0.49 | -1.21 | -0.72 | -0.12 | 272 |
| Cu(8, 3) | (111) {9} | 2.15 | 0.52 | -1.23 | -0.71 | -0.10 | 274 |
| 2-fold | | | | | | | |
| Cu(8, 6, 2) | (100) {8} | 2.48 | 0.36 | -1.02 | -0.67 | -0.11 | 180 |
| 3-fold | | | | | | | |
| Cu(12, 6) | (111) {9} | 2.85 | 0.21 | -0.59 | -0.38 | 0.04 | 133 |
| 4-fold | | | | | | | |
| Cu(4, 5) | (100) {5} | 2.03 | 1.00 | -0.60 | 0.40 | not calc. | not bond. |

^{a)} The cluster geometries are sketched in fig. 1. In between { } brackets are the number of metal-neighbour atoms of the central copper atom.

cially for the adsorption of hydrogen atoms on nickel clusters [17]. We compared Cu(5, 4, 1) clusters with a different number of copper atoms that were frozen, and in various arrangements. The results have been collected in tables 3 and 4. If we compare clusters that differ only in the second and third layer, we find that the steric repulsion, orbital interaction, adsorption energy, and optimum copper–nitrogen distance change only a little. Also the stretch frequency (ω) changes less than 10%. The effect when first-layer atoms are kept frozen is, however, much larger, the calculated energies are very different, the optimum copper–nitrogen distance has changed significantly, and ω has now changed by more than 10%. Apparently, computed molecular orbitals of the copper clusters are different whether or not the d orbitals of the first-layer atoms are frozen. This affects the repulsion with ammonia due to the d_{z^2} orbital of the central copper atom, the copper atom to which ammonia is directly bonded. The results in tables 3 and 4 seem to imply that freezing of the d orbitals in the second and third layer is possible. The electron-density difference plots shown in fig. 2 for Cu(5, 4, 1), Cu(5, 4, 1*) and Cu(5, 4*, 1*) indicate, however, that also the clusters with only frozen copper atoms in the second and third layer respond differently to ammonia adsorption. Because of this behaviour, and also because of the relative small reduction of the computational effort, we decided not to use the “mixed cluster approach”.

Table 5 shows, for the different absorption configurations and clusters, the steric repulsion, total orbital interaction and adsorption energy. Also the coordination number of ammonia, the number of nearest neighbours of the central copper atom, and the total adsorption energy including non-local corrections are mentioned. For the calculation of the optimum copper–nitrogen distance and ω , the non-local correction is not included. Comparison is made between clusters simulating the (100) surface and (111) surface. The clusters studied vary between 6 and 18 copper atoms (see fig. 1). Cluster sizes have been chosen such that on the clusters simulating the (100) and (111) surfaces, the copper atoms involved in the bond with ammonia have the same number of nearest-neighbour copper atoms as on the corresponding metal surface.

The steric repulsion decreases when a single copper atom acquires neighbours. This is due to a contraction of the electron density closer to the nuclei. The steric repulsion for the various clusters that simulate the (100) surface, i.e. Cu(1, 4, 1), Cu(5, 4, 1), Cu(5, 4, 5), and Cu(9, 4, 5), does not seem to have converged. However, we may conclude that it is only a few tenths of an electronvolt. The clusters Cu(9, 4, 5) and Cu(8, 6, 2), both simulating the (100) surface, have about the same number of atoms in the first layer, and about the same total number of atoms. Thus, they may be compared. It is interesting to note that the steric repulsion for twofold adsorption is larger than that of onefold adsorption, in accord with predictions of elementary quantum chemistry [18]. We find a strong increase in copper–nitrogen distance when the coordination of ammonia on the (111) surface is increased from onefold to threefold; compare Cu(7, 3) and Cu(12, 6). This is due to enhanced repulsion in the high-coordination site pushing the ammonia molecule away from the surface. Table 5 also shows that the steric repulsion is less for the (100) surface than for the (111) surface.

If we compare the orbital interaction for Cu(1, 4, 1), Cu(5, 4, 1), Cu(5, 4, 5), and Cu(9, 4, 5) clusters, we see that there is much larger change when the number of nearest neighbours of the central copper atom changes than when the size of the cluster changes. This indicates that the formation of the bond with the ammonia is a local process. The decrease of the orbital interaction with the number of nearest cluster-atom neighbours relates to the increased localization energy [5]. The orbital interaction energy for the (100) surface decreases (in the absolute sense) when the coordination of ammonia is increased. This apparently unexpected behaviour can be understood when one analyzes the electron-energy distribution in different coordination sites. As we illustrate below, this is most conveniently done using the concept of group orbitals [5,19,20]. We have shown previously for CO adsorption that the reduction of the Pauli repulsion forms a large part of the orbital interaction energy [21]. We find the same here.

Fig. 2a shows that between the nitrogen atom and the central copper atom there is a decrease of electron density near the copper atom and an increase

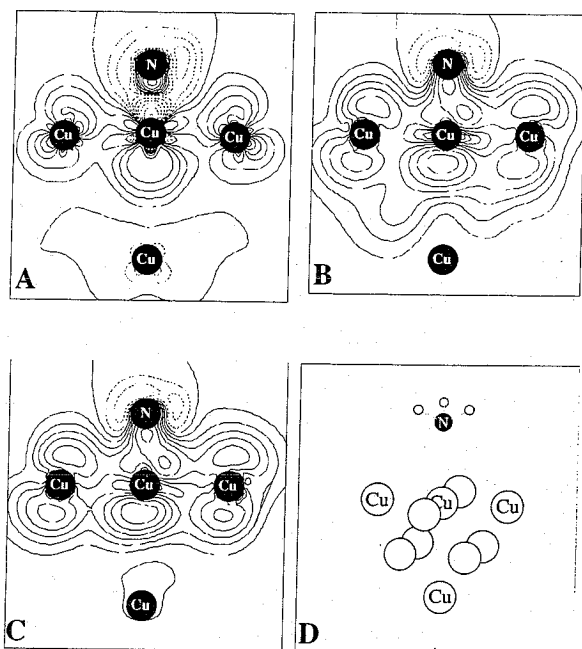


Fig. 2. Contour plots of the computed electron-density differences: (A) $\rho(\text{Cu}_{10}\text{NH}_3) - 10\rho(\text{Cu}) - \rho(\text{NH}_3)$ for $\text{Cu}(5, 4, 1)\text{-NH}_3$, (B) $\rho(\text{Cu}_9\text{Cu}^*\text{NH}_3) - 9\rho(\text{Cu}) - \rho(\text{Cu}^*) - \rho(\text{NH}_3)$ for $\text{Cu}(5, 4, 1^*)\text{-NH}_3$, and (C) $\rho(\text{Cu}_5\text{Cu}_3^*\text{NH}_3) - 5\rho(\text{Cu}) - 5\rho(\text{Cu}^*) - \rho(\text{NH}_3)$ for $\text{Cu}(5, 4^*, 1^*)\text{-NH}_3$. Dashed lines show a decrease, solid lines an increase of the electron density, except for the solid lines next to dashed lines which depict nodal surfaces. Subsequent contours correspond to ± 0.0000 , ± 0.0007 , ± 0.0016 , ± 0.0035 , ± 0.0071 , ± 0.0142 , ± 0.0287 , ± 0.0578 , ± 0.1167 , and ± 0.2348 electrons per \AA^3 . The four atoms shown in these figures correspond to the four labelled atoms shown in (D).

near the nitrogen atom. This latter feature can be traced back to the rehybridization of the lone-pair orbital of ammonia. A population analysis shows that this orbital gets more s character and less p character. Note that this kind of behaviour is absent in figs. 2b and 2c.

Both the steric repulsion and the orbital interaction energy drive the ammonia molecule towards the onefold site; the adsorption energy is clearly largest for the onefold site. It also seems that ammonia prefers the (100) to the (111) surface. This is mainly due to the difference in steric repulsion.

The calculated stretch frequency (ω) of ammonia on the various copper clusters shows a decrease when

moving from onefold to higher coordination. For onefold coordination, ω is higher on the (100) surface clusters than on the (111) surface clusters. For the (100) surface, the calculated frequencies compare rather well with the experimental value of 360 cm^{-1} [22]. We were unable to compare the calculated frequencies for the (111) surface with earlier calculations or measurements, but the results are comparable to those obtained from various other systems.

A detailed analysis of the interaction of ammonia with $\text{Cu}(9, 4, 5)$, $\text{Cu}(8, 6, 2)$, $\text{Cu}(7, 3)$, and $\text{Cu}(12, 6)$ is presented in figs. 3, 4 and 5. These figures show the local density of states (LDOS) before and after chemisorption, and the overlap-population density of states (OPDOS). For higher-coordination situations, the NH_3 σ -orbital interaction with the local density of states of totally symmetric surface orbital fragments is shown. For example, for the twofold coordination the s-atomic group orbital is

$$\Psi_g^s(\text{twofold}) = \frac{1}{\sqrt{2+2S}} [\varphi_1(s) + \varphi_2(s)]; \quad (2)$$

$\varphi_1(s)$ and $\varphi_2(s)$ are the atomic orbitals involved, S is their overlap. In threefold coordination, the corresponding group orbital becomes

$$\Psi_g^s(\text{threefold}) = \frac{1}{\sqrt{3+6S}} \times [\varphi_1(s) + \varphi_2(s) + \varphi_3(s)]. \quad (3)$$

As long as the copper-nitrogen distance does not change, one expects the average local density of states of the NH_3 σ orbital to be lower in high-coordination sites than in lower-coordination sites. Calculation of the orbital overlap with group orbitals Ψ_g^s shows that the interaction increases with $\approx \sqrt{N}$, the number of neighbour atoms. As we will discuss below, the NH_3 σ -orbital density should shift downwards because it forms, at low energies, part of a bonding orbital fragment. This can indeed be noted in fig. 4, which is computed for the same copper-nitrogen distance for both clusters.

Differences in the copper-nitrogen equilibrium distance dominate the LDOS features presented in figs. 3a and 3c. Fig. 3b demonstrates the computed dependence of the position of the two lowest of the σ LDOS peaks (P1 and P2) as shown in fig. 3a as

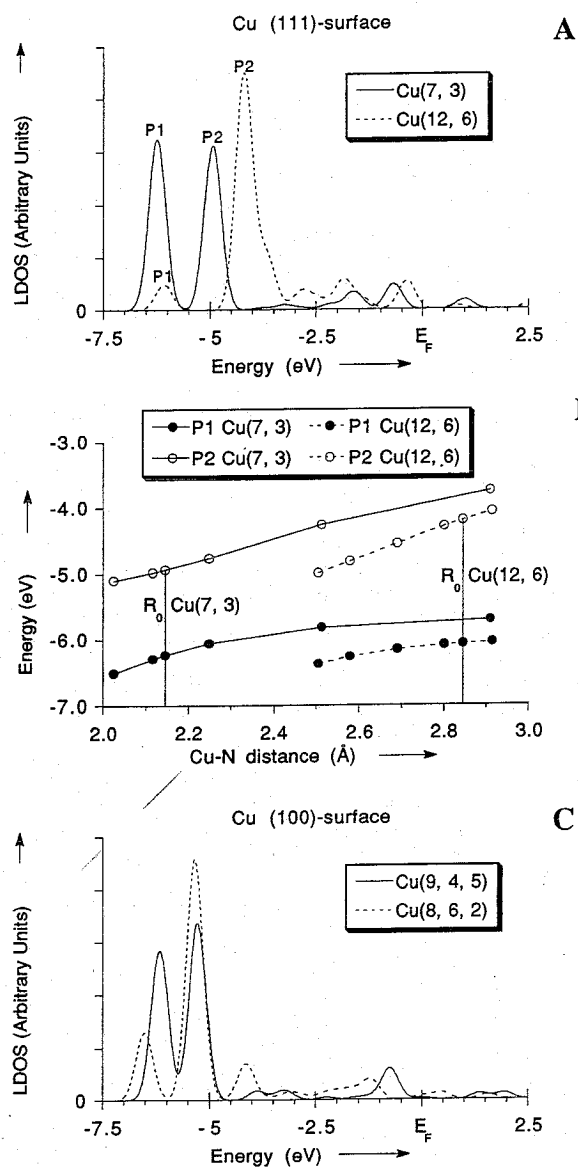


Fig. 3. Local density of states (LDOS) plot of the $\text{NH}_3 \sigma$ orbital after adsorption on the (111) surface clusters Cu(7, 3) and Cu(12, 6) (A). The position of the two lowest peaks (P1 and P2) in (A) as a function of copper-nitrogen distance, where R_0 is the equilibrium distance (B). LDOS plot of the $\text{NH}_3 \sigma$ orbital after adsorption on the (100) surface clusters Cu(9, 4, 5) and Cu(8, 6, 2) (C). Zero energy in (A) and (C) corresponds to the Fermi level (E_F).

a function of the copper-nitrogen distance. In figs. 3a and 3c, the $\text{NH}_3 \sigma$ LDOS are compared in low and high coordination on clusters simulating the

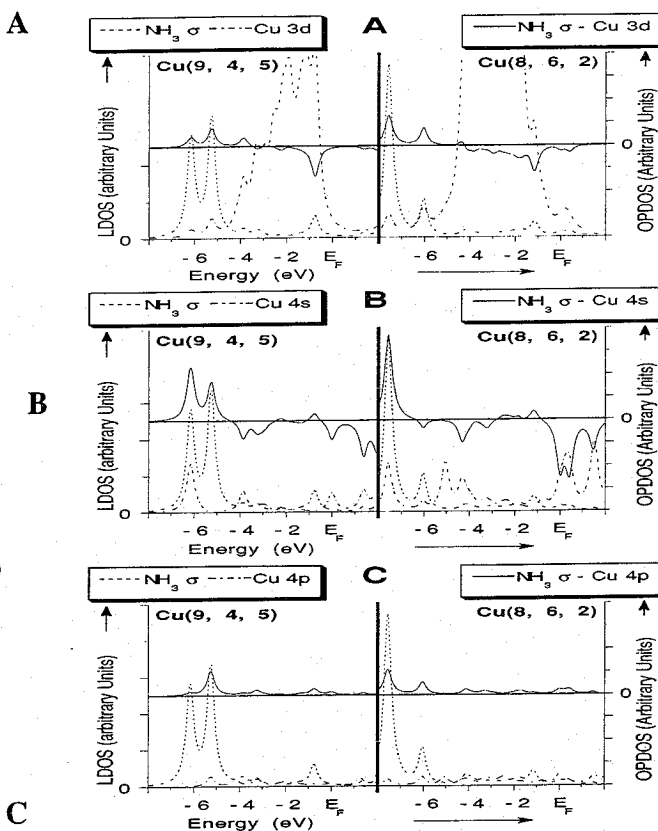


Fig. 4. Local density of states (LDOS) of the $\text{NH}_3 \sigma$ orbital, and the central copper 3d (A), 4s (B), and 4p (C) orbitals after adsorption together with the overlap population density of states (OPDOS) between both: on the left for the (100) surface cluster Cu(9, 4, 5), and on the right for the (111) surface cluster Cu(8, 6, 2). Zero energy in these figures corresponds to the Fermi level (E_F).

(100) and (111) surface, respectively, of an NH_3 adsorbed in its equilibrium position. As follows from fig. 3b, the larger equilibrium distance (R_0) for the higher-coordination sites dramatically affects the computed LDOS. The upward shift of $\text{NH}_3 \sigma$ LDOS in threefold coordination derives from the small orbital overlap at the large equilibrium distance found. Therefore, experimental information about the $\text{NH}_3 \sigma$ position with respect to the Fermi level should enable one to confirm the predicted preferential ammonia adsorption in the onefold position.

Similarly as in usual chemical bonding, the bond strength of surface-adsorbate bonds should be related to the population of bonding and anti-bonding

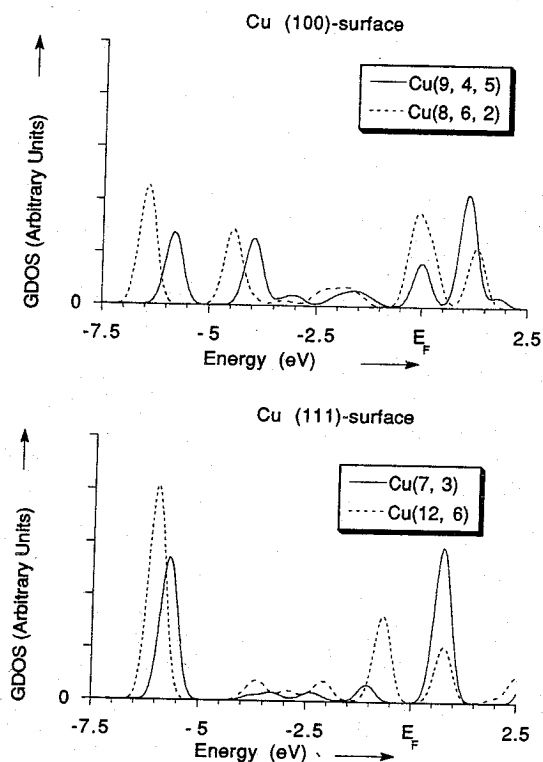


Fig. 5. Group orbital density of states (GDOS) plots of the central copper 4s orbital before ammonia adsorption for the (100) surface clusters Cu(9, 4, 5) and Cu(8, 6, 2), and for the (111) surface clusters Cu(7, 3) and Cu(12, 6). Zero energy in these figures corresponds to the Fermi level (E_F).

orbital fragments between adsorbate and surface [18,20,23,24]. Computation of the OPDOS enables us to analyze this. Results of such an analysis are presented in fig. 4. A positive sign implies a bonding interaction, and a negative sign an anti-bonding interaction. The calculations in fig. 4 refer to ammonia adsorbed in a onefold- and twofold-coordination site at the same copper-nitrogen distance. Only for such a case is comparison useful. A breakdown of the interaction with valence copper 4s, as well as 3d and 4p orbitals, is given. In table 6, the total orbital populations (in arbitrary units) are presented. The interaction with the s and p orbitals appears to be bonding but that with the d orbitals anti-bonding. This shows that the Pauli repulsion derives from the interaction with the occupied copper 3d atomic orbitals. This repulsion is larger in the high-coordi-

A

Table 6
Overlap population of the NH_3 σ orbital with selected copper orbitals (arbitrary units)

| copper orbital | Cu(9, 4, 5) | Cu(8, 6, 2) |
|----------------|-------------|-------------|
| 3d | -0.005 | -0.157 |
| 4s | 0.693 | 0.372 |
| 4p | 0.572 | 0.737 |
| total | 1.260 | 0.942 |

nation site than in the low-coordination site, as had also been found in table 5.

B

As the respective OPDOS indicate, there is not only a significant anti-bonding interaction with the copper d-valence orbitals, but also with the s-valence electrons. This is found notwithstanding the earlier observation that the overall interaction with the copper s-valence electrons is bonding. Note, however, that table 6 also shows that this bonding interaction is less in the high-coordination site than in the onefold adsorbed position. This result agrees with frontier-orbital arguments [5,18] that predict a correlation with the σ lower local density of states of s valence group orbitals around the Fermi level in a high-coordination site; the discrete nature of the group-orbital local-density of states (GDOS) in the clusters makes such a comparison useless. However, one observes from fig. 5 that a shift to an average lower energy is found for GDOS corresponding to high-coordination group orbitals. Returning to fig. 4, one sees that the peak position of the bonding σ -s adsorbate-surface s valence orbital interaction is lowest for the twofold-coordination site. This is, as mentioned earlier, partially due to the larger adsorbate-surface interaction, but also due to the lower corresponding GDOS in the higher-coordination site. This can be seen from the GDOS presented in fig. 5. As a consequence, the anti-bonding orbital fragments become occupied at lower energy in high-coordination sites than onefold. The weaker interaction energy with s valence atomic orbitals in high coordination then is a consequence.

The bond strength of onefold-adsorbed ammonia on comparable copper clusters is highest on each surface, from which one concludes that ammonia prefers onefold adsorption on copper (table 5). As far as we know, no experimental information on the adsorption geometry of ammonia on copper surfaces is

available. However, infrared adsorption spectra of CO adsorbed on copper show that CO also prefers the onefold configuration [25]. Because of the smaller back-donation contribution to the surface chemical bond, a contribution that tends to favour high-coordination sites [5], the predicted onefold adsorption geometry of ammonia is consistent with experimental observation of the adsorption site of CO. The predicted higher adsorption-energy value of onefold-adsorbed ammonia on the (100) surface than on the (111) surface agrees with the more open nature of that particular surface.

Interestingly, Chattopadhyay et al. [26] predict a slight preference for ammonia adsorbed onefold on the Ni(111) surface. This result of an *ab initio* CI calculation is consistent with our results. The partially occupied nickel d-valence electron band causes the differences in energy of ammonia adsorbed onefold or in higher-coordination sites to be less than on copper. Hermann et al. [27] found in cluster calculations for ammonia adsorbed on aluminium also a strong preference for onefold coordination. Pauli repulsion with the high electron-density of this s-p electron metal appears to be responsible as well as the decreased orbital-interaction energy, corresponding to the polarization energy in their calculation. As long as no reference can be made to larger cluster calculation or results of slab calculation, one cannot verify whether computed bond strengths have converged to the surface-limiting value. The separate analysis of repulsive and orbital interactions indicates that the computed value for onefold adsorption of ammonia, the Cu(5, 4, 5) cluster, may be close to its converged value. We have demonstrated that subdivision of clusters corresponding to models of the same surface makes useful qualitative comparisons possible.

4. Conclusions

Using the mixed cluster approach would at least give rise to a large error in the computed electron densities. If one wishes, nevertheless, to use this approximation, it is important to note that for a proper modelling of the copper surface, it is necessary that the atoms in the first layer are not kept frozen. The copper atoms in the second and following layers seem

to play a less important role, although they will still contribute to a more proper description of the metal surface. The total number of copper atoms that is kept frozen also does not seem to determine the accuracy of the mixed cluster approximation. Thus, Cu(5, 4*, 1*), with five frozen atoms, gives a smaller error than Cu(1+4*, 4, 1), with only four frozen atoms compared to Cu(5, 4, 1).

The calculated adsorption energy is probably quantitatively not precise, since we see a rather strong dependence on the size of the cluster. Nevertheless, there is clearly a trend towards onefold adsorption. This is true for the (100) and the (111) surface. Comparing the (100) surface with the (111) surface shows that in onefold adsorption, the steric repulsion is much less for the (100) surface while the orbital interaction is about the same.

With an OPDOS analysis, we were able to show that it is the interaction of ammonia with the copper d orbitals as well as the copper s-valence electrons which favours the onefold absorption site, while the interaction with the copper p orbitals favours the higher-coordination sites. Finally, we showed that it should be possible to confirm our predicted onefold adsorption geometry for ammonia on copper by determining the ammonia σ LDOS relative to the Fermi level.

Acknowledgement

We would like to thank the Theoretical Chemistry Group of the Free University of Amsterdam for their help. This work has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure and Scientific Research (NWO) and by The Royal Society. The computer time on the CDC Cyber 205 and the Cray Y-MP4/464 at SARA, Amsterdam, was financed by SURF/WGS from "Nationaal Fonds gebruik Supercomputers" (NFS) and the National Computing Facilities (NCF) Foundation under Project SC-183.

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