Molecular Orbital Studies on the Interaction of Single Transition Metal Atoms with NH_3 and H_2O Ligands

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The bond formation of 3d-metal atoms (Cr, Fe, Ni, Cu) with NH_3 and H_2O is investigated by an ab initio MO theory. In the case of NH_3, coupling occurs mainly through the HOMO $3a_1$-levels $\triangleq$ (N lone pair), whereas with H_2O the main contribution arises from σ-bond formation of the second highest occupied orbital ($3a_1 \triangleq \mathrm{O}2p_z$). Results on the bond energies, electron populations and orbital energies are in qualitatively good agreement with experimental data on the adsorptive properties of these molecules on transition metal surfaces.

1. Introduction

NH_3 and H_2O are quite common ligands in transition metal complex chemistry and are also the end products of important catalytic reactions occurring at transition metal surfaces. From the latter point of view the adsorption of these molecules has been studied quite extensively in the past [1, 2]. Although the bond strength is relatively weak, a series of photoemission studies, recently performed with both adsorbed NH_3 [3–10] as well as H_2O [11–15], demonstrated the occurrence of marked changes of the electronic properties of the ligands upon chemisorption. Experimental [16] as well as theoretical [17] experience has demonstrated that adsorption on extended metal surfaces can frequently rather well be modelled by systems in which one or several ligands are attached to a single metal atom. (A natural extension then consists in the 'cluster approach' where coupling to a small ensemble of metal atoms is considered [17].)

The first MO calculations in the present context were performed by Nicely and Dye [18] for NH_3/Li, where a bond energy of about 0.9 eV was predicted. Later Trenary et al. [19] used better basis sets to treat several Li complexes including NH_3 and H_2O as ligands. These authors [20] also showed that inclusion of electron correlation effects has only little influence on the theoretical properties (structure and stability) of the H_2O/Li system. More recently experimental UPS data for H_2O adsorbed on a Li surface were reported [21], which were also compared with ab initio MO calculations from the same group [22]. Finally the work by Hermann [23] has to be mentioned: He performed ab initio HF-calculations on the $Fe-NH_3$ system in order to model chemisorption of ammonia on iron surface.

The latter results will be of particular relevance to the present work, which deals with the application of an ab initio SCF MO method to the interactions between single Cr, Fe, Ni and Cu-atoms with NH_3 or H_2O. The data will then be compared with existing experimental results for corresponding adsorption systems.

2. Method and Models

The calculations were performed within the ab initio restricted Hartree-Fock (HF) approximation. Single zeta basis sets [24] for the NH_3 and H_2O ligands were used as in similar previous work [25–27]. The Ar cores of the transition metal atoms were replaced by effective potentials [28, 29], and their 3d, 4s and 4p-valence orbitals were taken into account by using [2s, 1p, 2d] basis sets according to Wachters [30] and Hay [31]. The $4s$ and $3d$ functions are composed of 4 and 6 primitives, respectively. The contraction coefficients were determined by HF calculations for the respective metal atom with $3d^{n-1}4s^1$ electronic configuration.

In order to study the influence of the basis set on bond distances and binding energies for clusters

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consisting of Ni, Cu with NH_3, H_2O, also calculations with better basis sets for the ligand atoms were performed: For N and O the [3s2p], and for H the [2s] sets were taken [32]. The resulting data will be referred to "better basis sets" calculations.

The mutual configurations of the metal atom and the ligand were assumed as shown in Figs. 1 a and 2 a, i. e. the electronegative atom of the ligand (N or O) couples to the metal atom whereas the H atoms are symmetrically directed away. Apart from the analogies with mononuclear complex compounds there is also experimental evidence for this geometry in the chemisorbed state: For example, analysis of angle resolved UPS data for NH_3/Ni(111) has demonstrated uniquely this type of bond formation [5]. With adsorbed H_2O, electron stimulated desorption [33] as well as vibrational spectroscopic data [34, 35] favour the proposed model, although in the latter case further complications may arise by the formation of hydrogen bonds.

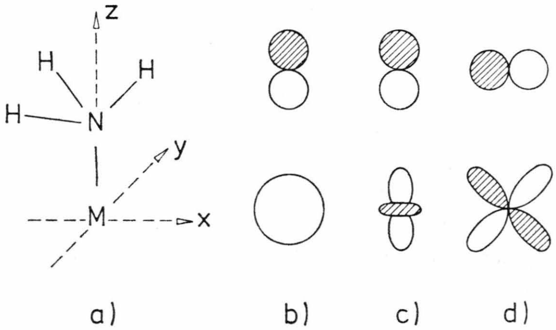

Fig. 1. Coupling of NH_3 to a transition metal atom.
a) Geometric configuration;
b)—d) Symmetry of orbital interactions:
b) $4s(M) - 3a_1(NH_3)$, c) $3d_z2(M) - 3a_1(NH_3)$,
d) $3d_{yz}/3d_{zx}(M) - 1e(NH_3)$.
Complete orbital pictures for NH_3 (after Ref. [48]) are shown in Figure 3.

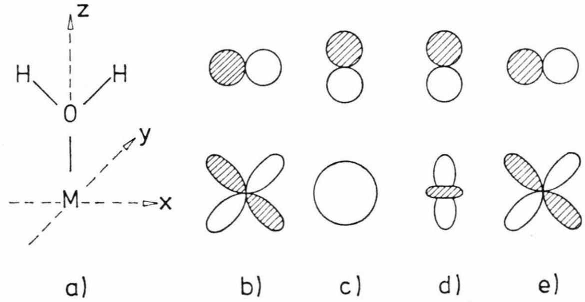

Fig. 2. Coupling of H_2O to a transition metal atom.
a) Geometric configuration;
b)—e) Symmetry of orbital interactions:
b) $3d_{yz}(M) - 1b_1(H_2O)$ (picture rotated by 90°),
c) $4s(M) - 3a_1(H_2O)$, d) $3d_z2(M) - 3a_1(H_2O)$,
e) $3d_{zx}(M) - 1b_2(H_2O)$.
Complete orbital pictures for H_2O (after Ref. [48]) are shown in Figure 4.

It was further assumed that the geometry of the ligand itself did not change upon coordination to the metal atom. The M-L distance was optimized to within ± 0.01 Å.

3. Results

Since the electron configuration of the transition metal was described by $3d^{n-1}4s^1$ [36], only those molecular orbitals derived from this configuration were calculated which exhibit the highest spin multiplicities. The 3d- and 4s-orbital energies of Cr, Fe, Ni and Cu as calculated on this basis by Clementi and Roetti [37] are listed in Table 1. The 3d orbital energies are strongly decreasing with increasing atomic number, whereas the 4s orbital energy is only slightly affected. In addition the 3d-orbitals are much more localized than the 4s-orbitals. Transition from a single atom to the bulk metal causes essentially the formation of a broad 4s-band spreading over the energy range above and below that of the 3d-band.

The theoretical results for the equilibrium M-L distance, dissociation energy, orbital energies and electron populations are represented in Table 2 for M-NH_3 and in Table 3 for M-H_2O. For these calculations it was assumed that the 3d-holes of the metal atom existed for Cr in all five d-orbitals, for Fe in the d_{xy}, $d_{x^2-y^2}$ and d_{z^2} orbitals, and for Ni in the d_{z^2}-orbital.

Previous calculations for Li-H_2O [19, 20] had shown that the use of better basis sets yields longer bond distances and smaller bond energies. The results of "better basis sets" calculations for Ni, Cu + NH_3, H_2O are listed in Table 4. Comparison with the corresponding data in Tables 2 and 3 shows that the same trend occurs with the present systems. In particular the bond energy with Cu is decreasing markedly by using the better basis set.

Table 1. The 3d and 4s orbital energies (eV) of transition metal atoms with the $3d^{n-1}4s^1$ electron configuration [37].

	Cr	Fe	Ni	Cu
4s	− 6.04	− 6.26	− 6.42	− 6.47
3d	− 10.16	− 11.06	− 12.44	− 13.35

Table 2. Theoretical data for M-NH_3 complex.
a) Equilibrium distances and bond energies

	Cr	Fe	Ni	Cu
r_{eq} [Å]	2.32	2.12	2.12	2.25
E_{bond} [eV]	0.43	0.98	0.65	0.33

b) Orbital energies [eV]

Level	Free NH_3					
	1) Theory	2) Exp.*	Cr	Fe	Ni	Cu
$3a_1$	−12.44	−10.9	−14.78	−15.25	−15.18	−14.98
$1e$	−17.39	−16.5	−19.05	−19.29	−19.23	−18.92
$2a_1$	−31.23	−27.7	−32.88	−33.11	−33.06	−32.77

* Negative ionisation potentials after Ref. [46].

c) Electron populations

	Free NH_3	Cr	Fe	Ni	Cu
H	0.752	0.731	0.726	0.722	0.724
N	7.743	7.771	7.764	7.763	7.750
M	—	6.037	8.060	10.071	11.078

Table 3. Theoretical data for M-OH_2 complexes.
a) Equilibrium distances and bond energies

	Cr	Fe	Ni	Cu
r_{eq} [Å]	2.17	2.07	2.06	2.17
E_b [eV]	0.66	0.64	0.74	0.44

b) Orbital energies

Level	Free H_2O					
	1) Theory	2) Exp.*	Cr	Fe	Ni	Cu
$1b_1$	−13.94	−12.6	−16.44	−16.44	−16.52	−16.09
$3a_1$	−14.95	−14.8	−18.11	−18.04	−18.21	−17.68
$1b_2$	−18.74	−18.7	−21.11	−21.06	−21.13	−20.72
$2a_1$	−35.82	−32.6	−38.14	−38.08	−36.16	−37.79

* Negative ionisation potentials after Ref. [47].

c) Electron populations

	Free H_2O	Cr	Fe	Ni	Cu
H	0.671	0.628	0.627	0.622	0.628
O	8.658	8.633	8.605	8.610	8.610
M	—	6.111	8.141	10.146	11.134

Table 4. The equilibrium distance and binding energy of Ni and Cu complexes with NH_3 and H_2O ligand from the better basis set calculation.

a) M-NH_3

	Ni	Cu
r_{eq} [Å]	2.33	2.68
E_{bind} [eV]	0.23	0.05

b) M-H_2O

	Ni	Cu
r_{eq} [Å]	2.33	2.85
E_{bind} [eV]	0.13	0.02

4. Discussion

4.1. Bond Energies

The calculated M-L bond dissociation energies will be compared with experimental adsorption energies for NH_3 and H_2O on transition metal surfaces. Unfortunately so far only a limited set of data is available:

The adsorption energy for NH_3 is in the range of 0.5 – 0.7 eV for both Fe [3, 4] and Ni [38] surfaces. For H_2O values of 0.60 eV on Ni [39] and of 0.35 eV on Cu [40] were reported. Both ligands exhibit a tendency for thermal dissociation at transition metal surfaces, but the indicated values are not influenced by such effects. These values are in fairly reasonable agreement with the theoretical data calculated with the single zeta basis sets. The experimental evidence that the adsorption energy of H_2O is about twice as large on Ni than on Cu is reproduced by the theory and is also in agreement with the experience with other ligands such as CO [41] or PF_3 [16].

The better basis set calculations (Table 4), on the other hand, yield much too low values for the bond energies.

This conclusion is in agreement with the results for H_2O/Li, where the near HF limit calculation predicts a bond energy of 0.56 eV [19] whereas 1.73 eV result from a single zeta calculation [22]. UPS experiments indicated that H_2O is molecularly held at a Li surface at room temperature [21], which requires an adsorption energy of at least about 1 eV, although no quantitative determination was made in that work.

On the basis of these findings it is concluded that for the present purpose the use of single zeta basis sets yields more reliable results than the better basis sets calculations. Further confirmation is obtained from an inspection of the calculated bond lengths:

Comparison of the data in Tables 2 and 3 for Cu and Ni shows that slightly shorter (~ 0.1 Å) bond lengths are predicted for Ni. Although no experimental data for adsorbed H_2O or NH_3 are available, LEED analysis of adsorbed CO revealed indeed this same tendency [42].

4.2. Electronic Properties-NH_3

If the electron populations listed in Table 2 for the free NH_3 molecule are used for the calculation of the dipole moment within a point charge model, a value of 2.1 Debye results, which agrees (in view of the crude approximation) fairly reasonably with the experimental value of 1.47 Debye [43]. Inspection of the other data in Table 2 shows that upon coupling to the metal atom, additional electronic charge is transferred from the H-atoms to N as well as M, suggesting that the cluster has an even larger dipole moment than the free NH_3 molecule. This picture supports similar conclusions reached previously on the basis of measurements of the variation of the work function upon NH_3 adsorption at a Fe(110) surface [4].

Inspection of Table 2 shows as a general tendency a lowering of the energies of the NH_3 orbitals upon coupling to the metal. This overall effect has to be ascribed to the slight electron transfer from the ligand to the metal, which causes stabilization of the ligand orbitals. As a consequence, the energies of the metal 3d orbitals (not shown here) are shifted upwards by about 1 eV. This effect is quite different to the situation with e.g. CO and PF_3 ligands [16], where the metal d-orbital energies are shifted downward since there the electropositive atom, C or P, is coupling to the metal atom.

For a more detailed discussion the calculated orbital energies have to be compared with experimental UPS data. The neglect of relaxation effects by using Koopmans' theorem instead of calculating the ionization potentials introduces of course an error of the order of several eV in the absolute energies. The situation is considerably improved if only relative energies, i.e. peak shifts, are considered. This problem was analyzed by Hermann [23] for a $FeNH_3$ cluster using ab initio Hartree Fock-calculations, where it turned out that the values for the peak shifts as calculated by the frozen orbital approach (= Koopmans) and by including relaxation differed by less than 0.7 eV for the three highest NH_3 derived levels.

The energetic separations between the highest levels of NH_3 as evaluated in the present work are compared in Table 5 with experimental UPS data as well as with the differences of the ionisation potentials calculated by Hermann [23]. Experimentally as well as theoretically the same trend is observed: The separation between the two highest levels ($3\,\alpha_1 \triangleq$ lone electron pair at the N atom and $1\,e \triangleq$ N-H bond) decreases upon coupling to the metal, which is ascribed to a "bonding shift" of the $3\,\alpha_1$ level by σ-bond formation between the N lone pair and the metal. On the other hand the $1\,e-2\,a_1$ separation remains constant – these levels are essentially not involved in the bond formation. The present calculations predict a decrease of $\Delta(3\,a_1-1\,e)$ by about 1 eV, which is in rather good agreement with the existing experimental data for Fe [3, 4] and Ni [5–8]. A much stronger effect resulted from Hermann's calculations [23] for the difference of the ionisation potentials as well as in the frozen orbital approximation, although a better approximation was used in this work. The improper handling of the relaxation problem as well as the neglect of correlation effects may be responsible for this difference between theory and experiment, which is obviously compensated in the present work by the use of a worse approximation.

However, an important difference between the present calculations and those of Ref. [23] has to be mentioned here: Hermann [23] treated the closed-shell singlet state ($^1A_1$), whereas the starting

Table 5. Separation (in eV) between orbital energies resp. ionisation potentials of the valence levels of NH_3.

	NH_3 (free)			$Cr\text{-}NH_3$		$Fe\text{-}NH_3$		$Ni\text{-}NH_3$		$Cu\text{-}NH_3$
	exp. [46]	[23]	this work	this work	exp. [3, 4]	[23]	this work	exp. [5]	this work	this work
$(3a_1 - 1\ )$	5.6	6.3	5.0	4.3	4.5	2.6	4.0	3.9	4.0	3.9
$(1e\ - 2a_1)$	11.2	13.6	13.8	13.8		13.8	13.8	11	13.8	13.9

point here was an open shell

$$\mathrm{Fe}\ d^7s^1\,(=d_{yz}^2\,d_{zx}^2\,d_{xy}^1\,d_{x^2-y^2}^1\,d_{z^2}^1\,4s^1)$$

configuration. For comparison also calculations for the Fe d^6s^2 closed shell were performed: The results were in qualitatively good agreement with Hermann's conclusions. With this configuration the electron repulsion is weaker than in the Fe d^7s^1 case. As a consequence the 3d energy is lower and the NH_3-$3\,a_1$ level interacts strongly with the d_{z^2}-level. It turned out, however, that the total energy of the Fe – NH_3 system is higher in this case than for the Fe d^7s^1 configuration, i. e. it represents an excited state. It was therefore felt that a better description is obtained by the chosen electronic configuration.

The types of orbital interactions are illustrated schematically in Fig. 1: It turned out that the $3\,a_1 \rightarrow 4s$ interaction is stronger than that between the $3\,a_1$ and $3d_{z^2}$ orbitals with the exception of Cu, where the situation is reversed since the Cu $3d_{z^2}$ lies energetically closer to the $3\,a_1$ level (see Table 1). A bonding interaction between the 1e orbital and the M d_{yz} and d_{xz} states, as illustrated by Fig. 1 d, is very weak because of only small overlap. The interaction of the NH_3 $2\,a_1$ level with the metal orbitals is, on the other hand, very weak since the energy differences are large: This is the reason why the $1\,e - 2\,a_1$ separation remains constant upon bond formation. The variations of the orbital energies of the ligand upon coupling to a metal atom as shown in Fig. 3 are illustrating the overall picture of the bond formation.

4.3. *Electronic Properties – H_2O*

The dipole moment for free H_2O calculated from the electron populations in Table 2 agrees exactly with the experimental value (1.85 Debye), which result should, however, not be overestimated. Coupling to a metal causes again electron transfer from the ligand to the metal atom, whereby the effect should be roughly about twice as large as with NH_3. No reliable work function data for H_2O adsorbed on 3d metals are available since in these cases always complications by possible dissociation may arise. As a consequence the general lowering of the H_2O derived orbital energies (Table 3) is even more pronounced than with NH_3. Inspection of the energy differences between the highest orbitals (Table 6) shows, however, a different tendency:

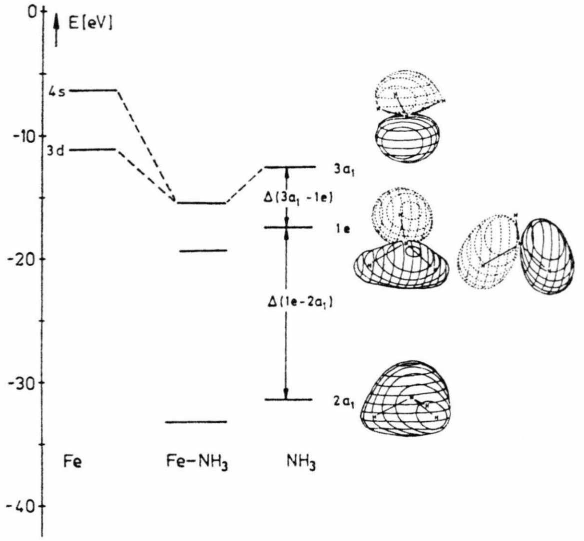

Fig. 3. Energy level diagram illustrating the bond formation for Fe-NH_3.

Table 6. Separation (in eV) between orbital energies resp. ionisation potentials of the valence levels of H_2O.

	H_2O (free)		Cr	Fe	Ni	Cu
	exp [47]	this work				
$(1b_1 - 3a_1)$	2.2	1.0	1.7	1.6	1.7	1.6
$(3a_1 - 1b_2)$	3.9	3.8	3.0	3.0	2.9	3.1

The energetic separation between the two highest MO's, $(3\,a_1 - 1\,b_2)$ should decrease as sketched schematically in Figure 4. The qualitative reason for this effect can easily be seen from Figure 2. The HOMO $1\,b_1$ level of H_2O has essentially O $2p_y$ ($\triangleq$lone pair) character and can only interact with the localized M d_{yz}-orbital. Since the resulting overlap is small, also the lowering in energy of the resulting bonding level will be small. The $H_2O - 3\,a_1$ level, on the other hand, exhibits pronounced O $2p_z$-character and forms therefore an appreciably strong σ-bond with the M 4s and $3d_{z^2}$ orbitals leading to a strong downward shift: $\Delta(1\,b_1 - 3\,a_1)$ will increase. Finally, the H_2O $1\,b_2$ level has largely O $2p_x$-character and will therefore only weakly interact with the M $3d_{zx}$-state (similarly as the $1\,b_1 \rightarrow d_{yz}$ interaction): $\Delta(3\,a_1 - 1\,b_2)$ will become smaller.

Unfortunately no reliable comparison with existing UPS data for H_2O absorbed on 3d-metals [11 – 15] can be made: These measurements have either

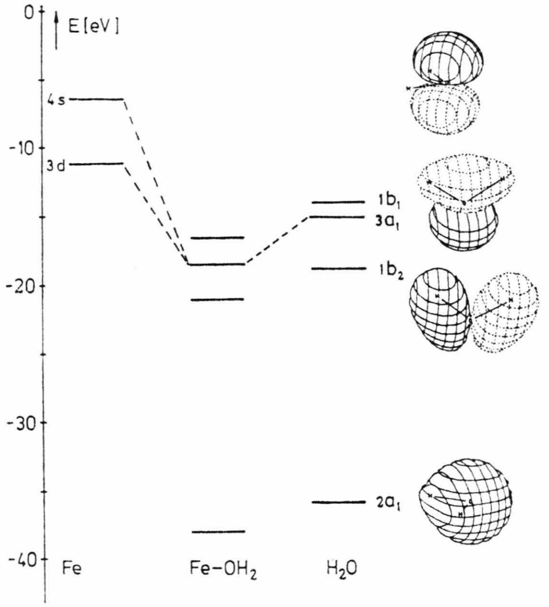

Fig. 4. Energy level diagram illustrating the bond formation for Fe-OH_2.

been performed with condensed multilayers, or strong interference with adsorbed O (from dissociation of H_2O) occurs. The only data in the monolayer range, where dissociation can be ruled out, were obtained for H_2O/Pt(111) [14]. There is a small but distinct increase of the $1\,b_1 - 3\,a_1$ separation, whereas the $3\,a_1 - 1\,b_2$ energy difference remains practically unaffected. The thermal desorption spectra demonstrate, however, that in the coverage range investigated by UPS already appreciable interactions between the adsorbed molecules exist, which is also supported by vibrational spectroscopic data [34]. These results may therefore only be regarded as a qualitative hint for the validity of the proposed mechanism of chemisorption bond formation.

Finally the results of some preliminary calculations for H_2S will be mentioned: UPS experiments with Ni [11] and Ru [44] revealed a pronounced tendency for dissociation, but in the latter case the molecularly adsorbed species was shown to exhibit peak separations which were completely identical (within 0.1 eV) to those of the free H_2S molecule. Calculations were performed for a Ni-SH_2 complex using the effective potential [28] and the single zeta basis set [45] for the S atom which was attached to the metal atom. It turned out that the equilibrium distance is much longer (3.8 Å) than in the case of H_2O. As a consequence of the weak overlap the bond energy is predicted to be rather small and no detectable bonding shift of the orbital energies should occur, which is in agreement with experiment *.

Acknowledgements

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* *Note added in proof*: Recent experiments by Benndorf et al. [49] with H_2O/Ni(110) at 150 K indicate an increase of the $(1b_1 - 3a_1)$ separation by 0.5 eV and a decrease of the $(3a_1 - 1b_2)$ separation by 0.6 eV upon adsorption. The adsorption energy was determined to be about 0.7 eV. These results are in good agreement with the data of Tables 3a and 6.

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