Molecular Orbital Calculations on the Interaction of PF_3 and CO with Ni and Cu Atoms

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The interaction of Ni and Cu atoms with PF_3 and CO ligands was investigated by means of ab initio MO calculations. Coupling occurs mainly through the HOMO ($8a_1$ for PF_3 and 5σ for CO) levels with the metal 4s and $3d_{z^2}$ orbitals, if the $3d^{n-1}\,4s^1$ electronic configuration of the metal atom is considered. The estimated M-PF_3 bond lengths are 2.0 Å for Ni and 2.5 Å for Cu. Calculations with Ni($3d^{10}$) revealed for PF_3 a more pronounced electron transfer to the ligand than for CO. The results are consistent with experimental UPS data for mononuclear complexes as well as corresponding adsorption systems. In particular, split-off d-states observed in UPS data for adsorbed PF_3 are attributed to the pronounced lowering of the 3d-orbital energy of the metal atom upon interaction with this electropositive ligand.

1. Introduction

The generally accepted mechanism of bond formation of a CO molecule either with single transition metal atoms or with an extended metal surface is illustrated by Fig. 1 a, namely by coupling of the highest occupied orbital (HOMO) of the ligang (5σ-donor) to the metal and by "back donation" of metallic d-electrons into the lowest unoccupied (LUMO) level ($2\pi^*$-acceptor). The lowering of the 5σ-orbital becomes quite evident from numerous UPS studies and is in the case of Ni and Cu, according to MO calculations [1–3], predominantly attributed to the interaction of the 5σ-level with the expanded 4s-levels of the metal. Differences in the bond strength are thereafter mainly due to the different degree of "back-donation": Whereas with bulk Ni the d-band extends beyond the Fermi level, with Cu its upper edge is about 2 eV below E_F [4, 5] which is also confirmed e.g. by EHMO [6] or SCF-X_α [7] calculations for Ni and Cu clusters.

Quite similar bonding properties are exhibited by PF_3 as illustrated by Figure 1 b. This molecule is a much more suitable candidate for UPS experiments than CO since the ionization potentials (I.P.) of its valence levels are well separated and can therefore be clearly resolved in the UP spectra (which is not the case with CO). PF_3 couples to transition metals mainly through the lone electron pair at the phosphorous atom ($8a_1$-level, HOMO) whose stabilization with respect to the next level (nearly degenerate $6e+1a_2$, corresponding to F lone pair) can therefore be regarded as representing an experimentally accessible measure for the electronic interaction between ligand and metal. Recently chemisorption of PF_3 on a whole series of transition metal surfaces was studied by UPS [8]. It turned out that the peak separation just mentioned, $\Delta\varepsilon = \text{I.P.}\ (8a_1) - \text{I.P.}\ (6e+1a_2)$, agreed well with corresponding data for mononuclear complex compounds, thus supporting the concept of "coordination chemistry of surfaces". For illustration Fig. 2 shows UPS data for free PF_3, as well as for $Ni(PF_3)_4$ and for PF_3 adsorbed on Ni(111) and Cu(110) surfaces. In the latter case the energy scale (with respect to the Fermi level E_F) was shifted by about 7 eV with respect to the vacuum level E_V in order to line up peak b ($= 6e+1a_2$, i.e. the F lone pair which is considered not to be affected by the bond formation). This

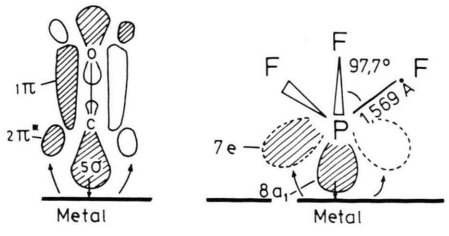

Fig. 1. Coupling schemes of a) CO, b) PF_3 to metals.

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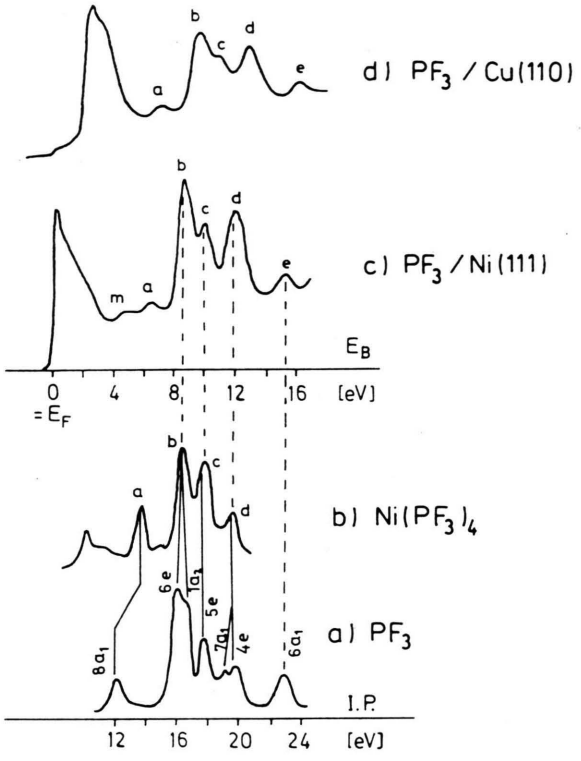

Fig. 2. Ultraviolet photoelectron spectra from a) free PF_3, b) $Ni(PF_3)_4$, c) PF_3 adsorbed on Ni(111), d) PF_3 adsorbed on Cu(110) (see Ref. [8]).

displacement takes account of the work function, $E_V - E_F$ (≈ 5 eV), as well as of the extra atomic relaxation energy caused by the presence of the metal surface. The lowering of the relative energy of the $8a_1$-level upon bond formation becomes quite evident: $\Delta\varepsilon = b - a$ is 2.8 eV for $Ni(PF_3)_4$ and 2.35 and 2.65 eV for adsorption on Ni and Cu, respectively, which has to be compared with $\Delta\varepsilon = 3.8$ eV for the free PF_3 molecule.

Preliminary ab initio MO calculations [9] for M-PF_3 complexes (M=Cr, Fe, Co, Ni) yielded $\Delta\varepsilon$ values which were in good agreement with the experimental data for chemisorbed PF_3 [8]. In these calculations the M-P distance was kept fixed at d = 2.0 Å which is about the actual bond length in $Ni(PF_3)_4$ (2.10 Å [10, 11]) or $HCo(PF_3)_4$ (2.05 Å [12]). If the same d value is taken for Cu-PF_3 the calculations will exhibit wrong results as will be shown below.

The present paper represents the systematic application of an ab initio MO theory to Ni-PF_3 and Cu-PF_3 clusters which will be used to discuss the adsorption of this ligand on the respective metal surfaces. The results will then be compared with the bonding properties of CO for which systems additional calculations were performed.

2. Method and Model

The calculations were performed within the ab initio restricted Hartree-Fock (HF) approximation. Effective potentials replacing the Ne core of the P atom and the Ar cores of Ni and Cu atoms were used [13, 14]. Accordingly the 3s and 3p valence orbitals of P and the 3d, 4s and 4p-orbitals for the metal atoms were explicitely taken into account. The basis sets of P were taken from [14], and the contraction coefficients were determined from SCF calculations. The basis sets for Ni and Cu [15, 16] consists of five primitives for 3d and of four primitives for the 4s-levels. The contraction coefficients were obtained from SCF calculations for the Nid^9s^1 triplet and the $Cud^{10}s^1$ doublet states which were the assumed electron configurations for the bulk metals [17]. These basis sets were extended by one p-function with exponent 0.12. Calculations with Nid^{10} closed-shell configurations were performed with contraction coefficients as determined for the Nid^{10} singlet state. One diffuse d-function was added according to Hay [16]. Gaussian basis sets contracted to a minimum set were used for the other atoms [18]. The present basis sets differ slightly from those applied in earlier work [9].

The M-PF_3 and M-CO clusters exhibit C_{3v} and linear symmetry, respectively. Values of the free PF_3 molecule were used for the P-F distance (1.57 Å) as well as for the F-P-F angle (98°) [19]. The C-O distance was taken as 1.15 Å. The M-P and M-C distances were varied.

Although previous ab initio MO calculations have demonstrated the usefulness of a single atom representation for a metal surface, additional calculations were also performed for linear M_B-M_A-CO systems containing two metal atoms. In this case the M_A-M_B and M_A-C distances were taken as 1.5 and 1.84 Å, respectively.

3. Results and Discussion

3.1. Interaction of Ni-$3d^9 4s^1$ and Cu-$3d^{10} 4s^1$ with PF_3 and CO

Since the valence electron configurations of Ni and Cu metals were assumed to be represented by

$3d^9 4s^1$ and $3d^{10} s^1$ configurations, respectively [17], only the molecular states with highest spin multiplicities were calculated. This procedure is believed to approach the actual situation of an extended metal surface. The HF orbital energies of the free metal atoms with these electronic configurations as calculated by Clementi and Roetti [20] are listed in Table 1. Thereafter the energy of the Cu 3d level is about 1 eV lower than that for the Ni 3d-states while the 4s orbital energies are similar. These 3d level positions are qualitatively consistent with the bulk 3d band energies stated above. The essential difference between an isolated metal atom and its bulk metallic state consists in the fact that in the former case the 4s orbital has the highest energy whereas in the latter the 4s-band spreads widely over the range of the 3d-bands.

Since the metal and the ligand orbitals retain much of their character after bond formation the notation for the free species will be used throughout. Orbital energies and electron populations as calculated as a function of the M-P distance are listed in Tables 2 and 3, whereby the notations $d_\pi \triangleq d_{zx}$, d_{yz} and $d_\delta \triangleq d_{xy}$, $d_{x^2-y^2}$ were used. The single hole in Ni was assumed to be in the d_{z^2} level. Accordingly the 3d-orbital energies split into three sublevels. For Ni the singly occupied d_{z^2} orbital has a lower energy than the other d-orbitals, whereas with Cu (double occupancy of d_{z^2}) just the reverse is the case. The 3d orbital energies of the free metal atoms calculated by the present basis sets are higher than those listed in Table 1. The calculated results for the free PF_3 molecule are in reasonable agreement with previous theoretical results [21] as well as experimental UPS data [22] (if a constant relaxation shift is assumed). In particular, the calculated separation between the $8a_1$ and $1a_2$ orbitals, $\Delta\varepsilon = 3.70$ eV, agrees well with the experimental value of 3.8 eV.

Tables 2 and 3 show that approaching of PF_3 to the metal atom causes a lowering of all orbital energies. According to elementary rules of quantum chemistry maximum interactions between two orbitals will occur if they have similar energy and strongly overlap. The HOMO of Pf_3, $8a_1$, lies near the metal orbitals and experiences a pronounced overlap. Accordingly appreciable stabilization of this orbital due to bonding interaction with the metal $3d_{z^2}$ and 4s levels occurs, whereas the other ligand levels are nearly non-affected which agrees with general experimental experience [8].

	Ni	Cu
4s	− 6.42	− 6.47
3d	− 12.44	− 13.35

Table 1. 3d and 4s orbital energies [eV] of Ni $3d^9 s^1$ and Cu $3d^{10} s^1$ configurations [20].

Table 2.

a) Orbital energies [eV] of Ni-PF_3 at various Ni-P distances d[Å].

State/d	2.0	2.25	2.5	3.0	∞
4s	− 6.04	− 5.95	− 5.95	− 6.13	− 6.02
$3d_{z^2}$	− 15.93	− 14.95	− 14.32	− 13.81	− 13.34
$3d_\pi$	− 14.60	− 13.32	− 12.55	− 11.94	− 11.45
$3d_\delta$	− 13.45	− 12.21	− 11.44	− 10.82	− 10.34
$8a_1$	− 15.36	− 14.97	− 14.58	− 13.96	− 13.49
$1a_2$	− 17.72	− 17.69	− 17.59	− 17.34	− 17.19
6e	− 17.80	− 17.78	− 17.67	− 17.43	− 17.27
5e	− 18.85	− 18.80	− 18.69	− 18.45	− 18.32
4e	− 20.92	− 20.81	− 20.68	− 20.41	− 20.26
$7a_1$	− 21.31	− 21.20	− 21.02	− 20.65	− 20.33
$6a_1$	− 25.52	− 25.22	− 24.93	− 24.49	− 24.23

b) Electron populations of Ni-PF_3.

d	2.0	2.25	2.5	3.0	∞
F	9.483	9.485	9.488	9.495	9.500
P	3.723	3.665	3.611	3.548	3.500
Ni	9.827	9.880	9.925	9.968	10.000

Table 3.

a) Orbital energies (eV) of Cu-PF_3 at various Cu-P distances d[Å].

State/d	2.0	2.25	2.5	3.0	∞
4s	− 5.82	− 5.81	− 5.88	− 6.10	− 5.99
$3d_{z^2}$	− 13.15	− 12.69	− 12.24	− 11.79	− 11.35
$3d_\pi$	− 15.11	− 13.61	− 12.67	− 11.89	− 11.35
$3d_\delta$	− 14.94	− 13.51	− 12.60	− 11.86	− 11.35
$8a_1$	− 16.76	− 15.55	− 14.79	− 13.95	− 13.49
$1a_2$	− 17.77	− 17.68	− 17.54	− 17.29	− 17.19
6e	− 17.87	− 17.78	− 17.63	− 17.38	− 17.27
5e	− 18.90	− 18.79	− 18.65	− 18.40	− 18.32
4e	− 20.97	− 20.81	− 20.64	− 20.36	− 20.26
$7a_1$	− 21.41	− 21.20	− 20.97	− 20.59	− 20.33
$6a_1$	− 25.61	− 25.21	− 24.88	− 24.43	− 24.23

b) Electron populations of Cu-PF_3.

d	2.0	2.25	2.5	3.0	∞
F	9.482	9.485	9.489	9.496	9.500
P	3.692	3.648	3.603	3.546	3.500
Cu	10.863	10.897	10.930	10.966	11.000

The theoretical separation between $8a_1$ and $1a_2$, $\Delta\varepsilon$, is plotted in Fig. 3 as a function of the M-PF_3 distance d. Obviously $\Delta\varepsilon$ decreases more strongly with decreasing d in the case of Cu than for Ni. This effect is attributed to the fact that the $8a_1$ level lies nearer in energy to the 3d levels of Cu than of Ni as seen from Table 1. From this figure a smaller $\Delta\varepsilon$ for Cu than for Ni at a given distance d is predicted, whereas the experiment shows the opposite trend: $\Delta\varepsilon(\mathrm{Cu}) = 2.65$ eV and $\Delta\varepsilon(\mathrm{Ni}) = 2.35$ eV. This suggests that in fact the equilibrium distance (bond length) is larger for the Cu than for the Ni complex. This idea is supported by the following considerations: The metal $3d_{z^2}$ orbital is antibonding with respect to coupling with the $8a_1$-level: Since it is doubly occupied with Cu, but only singly occupied with Ni its repulsive effect will be stronger with Cu. This is also supported by the data of Tables 2 and 3, which show a more pronounced lowering of the $3d_{z^2}$-energy for Ni than for Cu. This closed-shell repulsion in the case of Cu suggests a larger bond distance.

Comparison of experimental and theoretical $\Delta\varepsilon$-values can now be tentatively used to estimate the actual bond distances: For Ni-PF_3 $\Delta\varepsilon_{\mathrm{exp}}$ becomes equal to $\Delta\varepsilon_{\mathrm{theor}}$ for $d \approx 2.0$ Å which agrees well with the experimental distance in $Ni(PF_3)_4$, d = 2.1 Å [10, 11]. In the case of Cu agreement of the theoretical and the experimental value (2.65 eV [8]) would be reached for $d \approx 2.5$ Å which reflects the trend discussed above. Although no experimental data for the Cu-PF_3 bond distance are available this conclusion is qualitatively supported by the following features: i) The M-CO distance for adsorption on Cu(100) is about 0.1 Å larger than that for adsorption on Ni(100), as derived from LEED intensity analysis [23]. ii) Recent MO calculations for M-NH_3 and M-OH_2 complexes yielded in both cases equilibrium distances which were 0.12 Å longer for Cu than for Ni [24]. Also the bond energies were found to be about twice as large for Ni than for Cu, which compares well the experimental experience on the adsorption energies of CO [25] as well as PF_3 [8] on Ni and Cu surfaces.

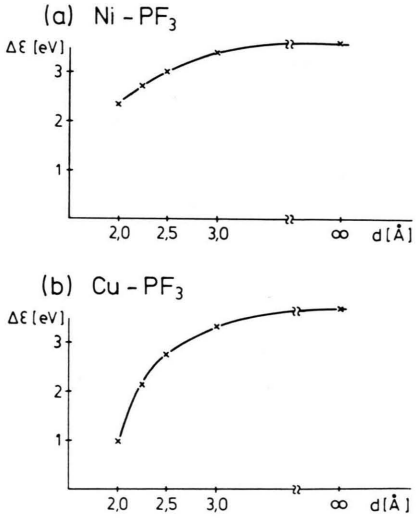

Fig. 3. Energetic separation $\Delta\varepsilon$ [eV] between the PF_3 $8a_1$ and $1a_2$-levels as a function of the M-P distance d. a) Ni-PF_3, b) Cu-PF_3.

Table 4.

a) Orbital energies [eV] of NiCO as a function of M-C distance d(Å).

State/d	1.84	2.0	2.5	3.0	∞
4s	− 5.38	− 5.28	− 5.29	− 5.54	− 6.02
$3d_{z^2}$	− 14.43	− 13.78	− 12.83	− 12.91	− 13.34
$3d_{\pi}$	− 13.06	− 12.23	− 11.05	− 11.05	− 11.45
$3d_{\delta}$	− 12.32	− 11.38	− 10.02	− 9.97	− 10.34
5σ	− 18.59	− 18.17	− 17.01	− 16.20	− 15.41
1π	− 19.80	− 19.78	− 19.52	− 19.18	− 18.79
4σ	− 22.98	− 22.93	− 22.64	− 22.28	− 21.89
3σ	− 43.60	− 43.69	− 43.56	− 43.21	− 42.80

b) Electron populations of Ni-CO.

d	1.84	2.0	2.5	3.0	∞
O	8.302	8.302	8.315	8.328	8.344
C	5.779	5.746	5.680	5.663	5.656
Ni	9.919	9.952	10.004	10.009	10.000

The calculated electron populations as also listed in Tables 2 and 3 indicate a slight transfer of electronic charge from the metal to the ligand which reflects the effect of "π-backdonation" of metallic d-electrons into the lowest empty orbital (π-acceptor 7e). Direct comparison with experimental work function changes is complicated: Free PF_3 has a considerable dipole moment (1.03 Debye) and should therefore per se cause an appreciable increase of the work function upon adsorption which effect should be enhanced by a net electron transfer from the metal to the ligand. In fact only work function increases by $\Delta\varphi = 0.3$ eV on Ni and $\Delta\varphi =$ 0.1 eV on Cu are observed [8].

The qualitative trend is, however, also shown by the theoretical results which predict a more pro-

Table 5.

a) Orbital energies [eV] of Cu-Co as a function of M-C distance d(Å).

State/d	1.84	2.0	2.5	3.0	∞
4s	− 5.18	− 5.13	− 5.24	− 5.51	− 5.99
$3d_{z^2}$	− 12.63	− 12.00	− 10.97	− 10.94	− 11.35
$3d_{\pi}$	− 13.61	− 12.67	− 11.15	− 10.98	− 11.35
$3d_{\delta}$	− 13.81	− 12.76	− 11.15	− 10.99	− 11.35
5σ	− 19.12	− 18.42	− 16.94	− 16.11	− 15.41
1π	− 20.00	− 19.86	− 19.46	− 19.13	− 18.79
4σ	− 23.24	− 23.03	− 22.57	− 22.23	− 21.89
3σ	− 43.84	− 43.79	− 43.43	− 43.16	− 42.80

b) Electron populations of Cu-CO.

d	1.84	2.0	2.5	3.0	∞
O	8.296	8.299	8.316	8.330	8.344
C	5.746	5.727	5.679	5.662	5.656
Cu	10.958	10.975	11.005	11.008	11.000

Table 6. Electron populations in M_B-M_A-CO clusters.

	M_B	M_A	C	O
Ni	10.143	9.773	5.788	8.296
Cu	11.187	10.763	5.765	8.285

nounced electron transfer for Ni than for Cu. This effect is related to the 3d level positions of Ni and Cu. The lowering of the 3d orbital energies upon interaction with PF_3 will be discussed in Section 3.3.

Orbital energies and electron populations for Ni-CO and Cu-CO are listed in Tables 5 and 6 as a function of the M-C distance. The overall trend is quite similar as in the case of PF_3. Determination of the equilibrium distance by comparison of the $5\sigma - 1\pi$ level separation with experimental UPS data in a similar way as done with PF_3 is not possible in this case, however, since both peaks overlap in the photoemission spectra.

CO adsorption increases the work function on Ni by 1.3 eV, but decreases it on Cu by about 0.3 eV. The findings for Ni are qualitatively consistent with the pronounced electron transfer to CO at an M-C distance of 1.84 Å which is the equilibrium distance in $Ni(CO)_4$ as well as close to the distance for CO adsorbed on a Ni(100) surface [23]. The analogy with PF_3 as well as the experimental LEED evidence [23] suggests that the Cu-C distance is longer, probably around 2.0 Å, for which value only a slight electron transfer (~ 0.02e) to the ligand is predicted. Again the 3d orbital energies are lowered, but to a lesser extend than in the case of PF_3.

3.2. Interaction of Ni_2 and Cu_2 with CO

In order to get some information on the range of the metal-ligand interactions a series of further calculations was performed for linear clusters of the type M_B-M_A-CO. The resulting data for the orbital energies are illustrated by Figure 4. Levels marked by small arrows are singly occupied while all others are doubly occupied. With the free M_2 molecule each d-level has equal contributions from both metal atoms. These d-levels, however, split into two groups with the M_2CO clusters, which are localized at the M_A and M_B atoms as indicated. The d-levels of the M_A atom (which neighbors the ligand) are shifted downward in a manner similar to the mononuclear compounds, whereas the d-

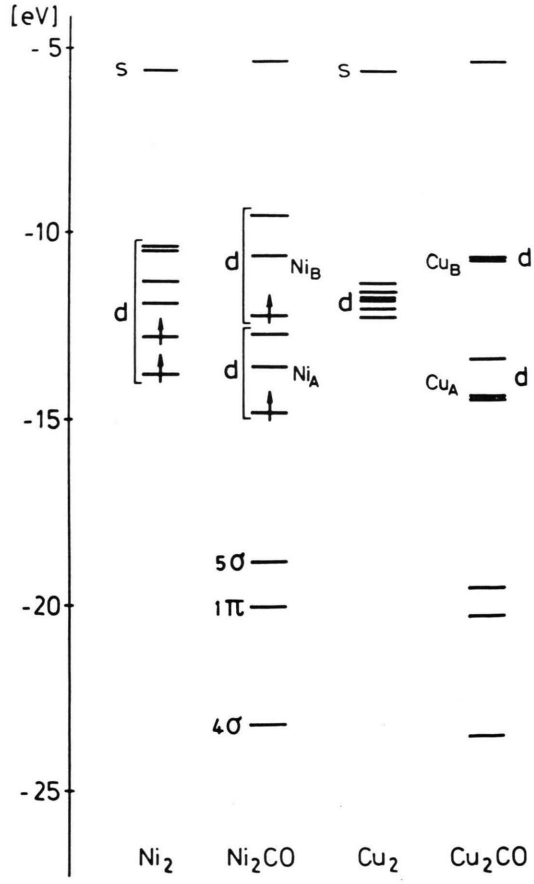

Fig. 4. Orbital energies for Ni_2, Ni_B-Ni_A-CO, Cu_2, and Cu_B-Cu_A. Levels denoted by ↑ are singly occupied while all others are doubly occupied.

orbital energies of the M_B atom are nearly not affected. That means that the influence of the ligand is more or less restricted to that metal atom to which it is attached thus justifying the local picture of bond formation as well as the single atom representation of a metal surface. Also the magnitudes of the level shifts (for both the CO ligand and the M_A atom) are rather similar to the results of the calculations with only a single atom. The charge distribution, however, exhibits effects which are also extending to the M_B atom as can be seen from the electron populations listed in Table 6: Electronic charge is transferred from the M_A atom to the ligand as well as to the M_B atom. Qualitatively similar conclusions were reached by Herrmann and Bagus [26] for a Ni_2-CO cluster and by Kadura and Opitz [27] for linear Fe_n-CO ($n=1$ to 10) clusters.

3.3. *Interaction of $Ni3d^{10}$ with PF_3 and CO*

So far the Ni atom was described by a $3d^94s^1$ electronic configuration in order to simulate the bulk electronic structure by a single metal atom or a diatomic cluster. However a $3d^{10}$ closed shell configuration is more appropriate for the description of mononuclear Ni complex compounds. Therefore additional calculations were performed for Ni-PF_3 ($d=2.10$ Å) and for Ni-CO ($d=1.84$ Å) by using this closed-shell configuration. The results are listed in Table 7. In this case the ligand HOMO levels, $8a_1(PF_3)$ and $5\sigma(CO)$, respectively, interact mainly with the localized $3d_{z^2}$-orbital, in contrast to the properties of the $3d^94s^1$ configuration. The $8a_1-1a_2$ separation for Ni-PF_3 turns out to be somewhat larger ($\Delta\varepsilon=2.58$ eV) than in the previous calculations using the same d ($\Delta\varepsilon=2.51$ eV). This effect could possibly account for the difference in the experimental $\Delta\varepsilon$-values between $Ni(PF_3)_4$ and PF_3 adsorbed on Ni(111) (2.8 and 2.35 eV, respectively [8]). Similar, but even more pronounced differences are found in the case of CO $\Delta(5\sigma-1\pi)=1.77$ eV for d^{10} and 1.21 eV for d^9s^1 configurations.

Table 7. Data for Ni(d^{10})-PF_3 and Ni(d^{10})-CO.

a) Orbital energies.

State	Ni-PF_3	State	Ni-CO
$3d_{z^2}$	− 10.01	$3d_{z^2}$	− 9.32
$3d_\pi$	− 10.62	$3d_\pi$	− 9.74
$3d_\delta$	− 10.53	$3d_\delta$	− 10.01
$8a_1$	− 14.18	5σ	− 16.43
$1a_2$	− 16.76	1π	− 18.20
6e	− 16.85	4σ	− 21.22
5e	− 17.90	3σ	− 41.80
4e	− 19.92		
$7a_1$	− 20.06		
$6a_1$	− 24.04		

b) Electron populations.

	Ni-PF_3		Ni-CO
F	9.489	O	8.347
P	3.711	C	5.725
Ni	9.821	Ni	9.928

The electron population data in Table 7b reveal a more pronounced electron transfer from Ni to PF_3 than to CO (0.18 e vs. 0.08 e), quite in analogy to the results for the Ni$3d^94s^1$ configuration. This confirms the general chemical experience whereafter PF_3 is a stronger electron acceptor than CO [28]. These effects are also reflected in the 3d orbital energies of the metal atom. As can be seen from Table 7a this energy is lowered from − 7.96 eV for the free Ni$3d^{10}$ atom to average values of − 10.46 eV in Ni-PF_3 and of − 9.76 eV in Ni-CO. These latter data compare qualitatively well with the experimental negative ionisation potentials of the 3d-states in $Ni(PF_3)_4$ and $Ni(CO)_4$ (− 10.11 eV and − 9.4 eV, respectively). As outlined in section 3.1, a similar lowering of the 3d orbital energies also occurs with the Ni$3d^94s^1$ configuration. UPS data from PF_3 adsorbed on Ni (as well as Fe and Pd) metal surfaces exhibit indeed the appearance of a "split-off" d-state (peak "m" in Fig. 2) below the bottom of the d-band [8], which in turn can be considered as additional justification for the "surface molecule" approach. In this picture this lowering of the 3d-energy can simply be regarded as being the consequence of the interaction of an electropositive atom (P) with the surface. Accordingly such an effect also occurs with CO (but less pronounced), but not if coupling takes place through an electronegative atom such as N or O as in the case of NH_3 or H_2O [24].

4. Summary and Conclusions

In order to model chemisorption on metal surfaces and bond formation in mononuclear complex compounds the interaction of Ni and Cu atoms with PF_3 and CO ligands was treated by an ab initio

MO method. It was found that the HOMO ($8a_1$ for PF_3, 5σ for CO) levels are lowered in energy due to donor-type interaction with the metal which is consistent with general experience from UPS experiments. The metal surface was simulated by single atoms with $3d^94s^1$ (Ni) and $3d^{10}s^1$ (Cu) electronic configurations, respectively, and coupling takes place through the 4s and $3d_{z^2}$ levels. Calculations for linear M_B-M_A-CO clusters demonstrate that the influence of the ligand is essentially restricted to the neighboring metal atom, thus justifying the local picture of bond formation.

M-PF_3 distances are estimated to be around 2.0 Å for Ni and 2.5 Å for Cu by comparing the experimental ionization potentials with the orbital energies calculated as a function of the M-P distance. The different adsorption properties of Ni and Cu are mainly due to differences of their 3d levels.

Calculations with the $Ni3d^{10}$ closed-shell configuration were performed in order to simulate the electronic properties of $Ni(PF_3)_4$ and $Ni(CO)_4$. The results were qualitatively similar to those with the $3d^94s^1$ configuration and support the general chemical picture, whereafter electron transfer from the metal to the ligand is more pronounced with PF_3 than with CO. As a consequence a stronger lowering of the 3d orbital energy takes place with PF_3. A similar effect occurs with the $Ni3d^94s^1$ and $Cu3d^{10}4s^1$ configurations which is in agreement with the observation of "split-off" d-states below the d-bands in photoelectron spectra from PF_3 adsorbed on Ni, Fe and Pd surfaces.

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