PF₃, PF₂, and PF on Ni(111): Theoretical aspects of their chemisorption

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The chemisorption of PF_3, PF_2, and PF on Ni(111) is examined, using tight binding extended Hückel calculations on a three-layer model slab. We have studied various adsorption sites. Calculations indicate that PF_3 should be preferentially bound to the onefold on-top Ni sites, with P–F bonds azimuthally oriented over neighboring Ni atoms. PF_2 is indicated to bind in a "perpendicular" manner at a twofold bridging site or possibly at a threefold site; and PF to the threefold hollow sites. These calculations are in agreement with experimental findings. PF_3 remains a σ donor and a π acceptor (through backbonding) on the surface; in the bonding of PF_2 and PF the π interaction is more important.

The analogy between organometallic, coordination chemistry, and chemisorption on metal surfaces serves us in so many ways. Often, it provides us with a suggestion as to which chemisorption systems might be interesting to study.[1] For instance, PF_3 is a useful, common ligand.[2,3] It has played an important role in the development of organometallic and coordination chemistry, because it forms tractable complexes with nearly all transition elements.[4] Examples are $Ni(PF_3)_4$ and $Co(PF_3)_6$.[5,6] PF_3 is widely used as a ligand; its highly electron withdrawing fluorines lead to substantially enhanced backbonding and a stronger metal-phosphorus bond.[7] Its electronic structure allows σ donation through the highest occupied molecular orbital (HOMO), and π backdonation to its lowest unoccupied molecular orbital (LUMO) (P $3d$ or PF σ^* orbitals) from the appropriate metal d orbitals. The chemistry of PF_3 has been extensively reviewed by Nixon.[2] He also briefly mentioned chemisorption studies of PF_3 on metals.

There have been many experimental studies of the chemisorption of PF_3 on various metal surfaces, for instance those of Blyholder and Sheets,[8] Ertl and co-workers, and others.[9] They all drew the conclusion that PF_3 has the characteristics of a σ donor and a π acceptor. Concerning the theoretical aspects, several calculations have been carried out on PF_3 on different surfaces. Doyen's[10] result was consistent with on-top bonding of PF_3 on surface Ni atoms. Itoh and Ertl[11] used a molecular approach to calculate the interaction of PF_3 with Ni atoms. The result supported donor–acceptor bonding for PF_3.

The first discrete molecular PF_2 compound was reported by Kruck and Lang.[12] The molecule is $[(PF_3)_n M(PF_2)]_2$, where the PF_2 groups bridge the metals. Most organometallic phosphido ligands indeed are bridging, bonded to two metals. Some terminal phosphido complexes are known, but neither Ni nor F is bonded to the phosphorus.[13] The last fragment considered by us is PF. PF is not commonly known as a ligand in inorganic chemistry. However, μ_2,[14] μ_3,[15] μ_4 [16] bridging phosphinidene (PR) complexes are known.

Recently, Alvey and Yates[17] have investigated systematically the chemisorption of PF_3, PF_2, and PF using electron stimulated desorption ion angular distribution technique (ESDIAD). PF_2(ads) and PF(ads) are produced by dissociation of PF_3 on the surface, using electron irradiation.

Alvey and Yates have produced evidence for the preferred sites of adsorption of all three species.

In this work, an approximate molecular orbital scheme, the extended Hückel method, is used to understand the bonding of all three species on the Ni(111) surface. We are interested in whether PF_3 will retain its typical organometallic mode of bonding on the surface, whether PF_2 will bond to the bridging site or in another way, and where the PF fragment might sit on a metal surface. The calculations provide density of states (DOS) plots, as well as local or projected DOS contributions.[18] Another calculated index, the overlap population, shows the degree of bonding of two specified atoms. A positive number means a bonding interaction, while a negative number means an antibonding interaction. Furthermore, crystal orbital overlap population (COOP) plots tell us the bonding character and the relative bond strength of a certain bond as a function of the energy of the orbitals, weighting the DOS in each energy interval by its contribution to the overlap population. Our general approach is that of a fragment analysis. The system is divided into two fragments, consisting respectively of the surface and the absorbates, which are then interacted. This enables us to compare the changes between the bare surface, the absorbates, and the composite chemisorbed system. We begin with a study of the separate surface and absorbed molecule.

Ni(111) SURFACE

Nickel metal has a face-centered-cubic structure with $a = 3.52$ Å.[19] Its nearest neighbor contact is 2.49 Å. The Ni(111) face is a hexagonal surface. The adsorbate coverage used here is 1/4, which is the same as in the experiment done by Alvey and Yates.[17] With this coverage, no short distances between adsorbates are found. The coordinate system is as in 1. The z axis points along the P–Ni direction, perpendicular to the xy plane in the surface.

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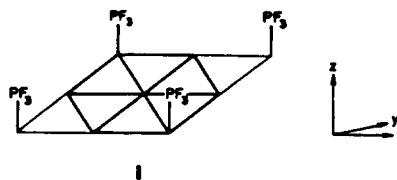
In order to achieve the best compromise between time of calculation and accuracy of the model, we have chosen a three-layer slab, with a one-sided coverage of the adsorbates. Previous work in our group has addressed the accuracy of three-layer and four-layer slab approximations and the coverage of one or both sides of the slab.[20] The arrangement of the three layer slab is shown in 2. Layers A and C represent the surface, while B represents the bulk. Adsorbates will be put on side A in the calculations.

2
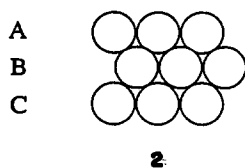
The unit cell, with 1/4 coverage, now becomes a $p(2 \times 2)$ hexagonal cell, as indicated in 1.

Let us first look at the bare surface itself. Table I collects some results of the calculations.

As the surface atoms have fewer nearest neighbors, these states are less dispersed than the bulk states. Consequently, if the Fermi level falls above the midpoint of the d block, as in the case of nickel, the nickel surface is negatively charged with respect to the bulk. This has been given a simple explanation in a previous paper from our group[20] and in the work of others.[21] The overlap populations indicate the surface atoms are more strongly bound to each other.

Figure 1 shows the total DOS of the nickel surface and some orbital contributions to it. s and p orbitals, being more dispersed, run from -12 to 7 eV. d orbitals run from -12 to -8 eV and more contracted; 30% of the s band is filled at the Fermi level. Note the substantial penetration of the s and p bands into the d bands. The Ni surface orbital populations are $d^{9.2}s^{0.6}p^{0.2}$, which is similar to the usually assumed $d^{9}s^{1}$ for Ni metal.

ADSORBED PF₃

In any discussion or calculation of phosphorus, attention must be paid to the vexing question of the possible participation of P $3d$ orbitals.[4,22–25] A calculation that includes them will of course have them contribute to the bonding. The question is not whether P $3d$ functions mix in or participate (they do) but whether they play an essential role. What is deemed to be essential seems to be, to some degree, a function of the observer. Our position in the past[26] and now is a conservative one—$3d$ orbitals certainly will participate, but we doubt if they will do so importantly. So we leave them out, at least in this first analysis of the problem. Later on we

will put the d orbitals into the calculations, and see what the effect will be.

The PF₃ radical is pyramidal, as shown in 3. The P–F bond distance is 1.57 Å and the F–P–F angle is 98°.[27]

3
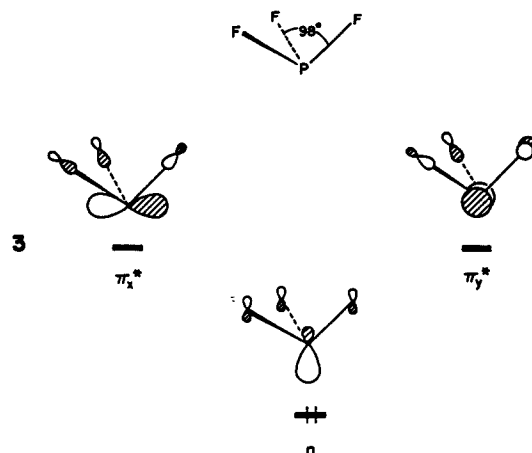
There are 16 orbitals in the PF₃ molecule. The three most important ones, the frontier orbitals, are shown in 3. These three orbitals are responsible for the σ donor and π acceptor properties of the molecule. The highest occupied molecular orbital (HOMO) is a phosphorus lone pair, which we will call "n." Its energy level is -13.4 eV. This orbital is only 1.2 eV lower than the bottom of the nickel d band, so it is expected to interact well with the appropriate metal d orbitals on the surface. The lowest unoccupied molecular orbital (LUMO) consists of a pair of degenerate π^* (π_x^* and π_y^*) orbitals, carrying larger coefficients on the phosphorus. These are unexpectedly high in energy, which does not bode well for their eventual role as π acceptors on a surface. Other orbitals, which are below the HOMO or above the LUMO, are expected to have only a very small interaction with the metal, since their energies are too far removed from the metal d states. This will be verified later on, in the DOS plots.

There are three adsorption sites which we are going to investigate: on-top, twofold, and threefold. These are shown in two views (top and from the side) in 4.

4
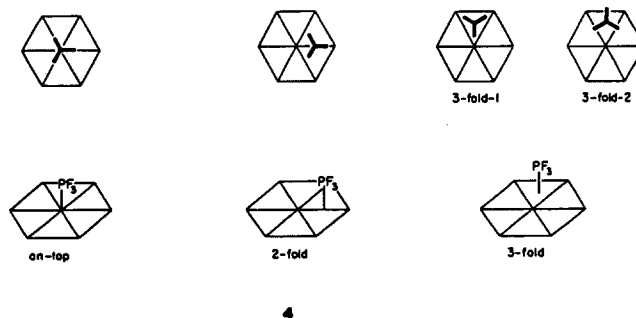
In each site, one could study a range of PF₃ rotations around the surface-P axis. But for on-top and twofold adsorption, the rotation barrier in question is sixfold and unlikely to be of significant magnitude. So we report only one conformation, that indicated in 4 for these, and two conformations for the threefold site. The Ni–P distance throughout the calculation is kept at 2.0 Å,[6,7,11] which is approximately the actual bond
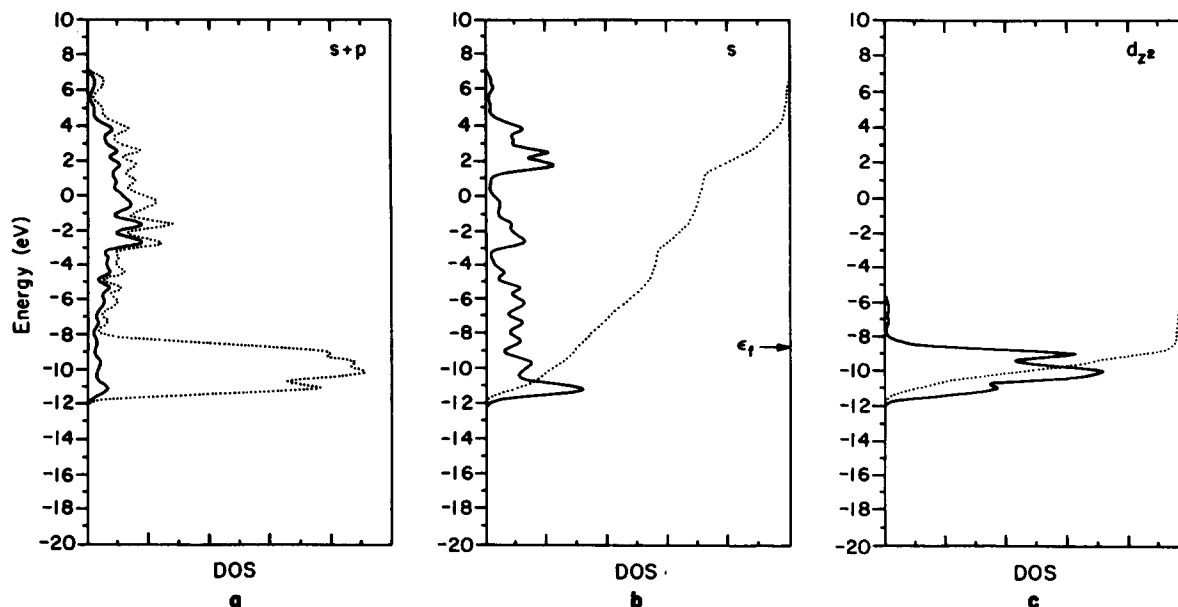
TABLE I. Calculation results of the bare Ni(111) surface.

Overlap populations between nickels:	
Surface–surface	0.10
Surface–bulk	0.06
Bulk–bulk	0.08
Net charges on nickel atoms:	
Layer A (surface)	− 0.09
Layer B	+ 0.18
Layer C (surface)	− 0.09

FIG. 1. (a) Projected s and p orbitals (solid line) of the surface Ni atoms; dotted line indicates total DOS. (b) Projection of s orbitals of the surface Ni atoms; dotted line is its integral. The s contributions are magnified 5× relative to panel a. (c) Projection of d_{z^2} orbitals of the surface Ni atoms; dotted line is its integral. The magnification is 5x.

length of $Ni(PF_3)_4$. Further details of the computations are given in the text and in the Appendix.

Table II collects some important calculated results for these sites. First let us look at the binding energies (B.E.) of the different sites. These energy differences between the composite system and separated surface + PF_3 monolayer measure the stabilization of the whole system upon chemisorption. Positive binding energy denotes attraction between the metal surface and the adsorbate, while a negative B.E.

TABLE II. Consequences of approaching PF_3 to $Ni(111)$ surface in different orientations.

	on-top	2-fold	3-fold-1	3-fold-2
Energies:				
ϵ_f [a]	− 8.56	− 8.56	− 8.53	− 8.56
B.E.[b]	3.09	2.59	1.37	2.25
Overlap populations:				
Ni–P	0.73	0.40	0.28	0.34
P–F [c]	0.47	0.48	0.49	0.49
Ni–Ni[d]	0.10	0.08	0.08	0.08
Ni–Ni[e]	0.05	0.03	0.05	0.05
Ni_b–Ni_b [f]	0.11	0.11	0.11	0.11
Ni_b–Ni_s [g]	0.10	0.10	0.10	0.10

[a] Fermi energy in eV.
[b] Binding energy $= [E(\text{slab}) + E(PF_3)] − E(\text{system})$, in eV.
[c] Molecular overlap population for P–F $= 0.44$ in free PF_3.
[d] Overlap population between the surface Ni atoms.
[e] Overlap population between the bonded Ni and the other surface Ni atoms.
[f] $Ni_b = $ bulk Ni.
[g] $Ni_s = $ surface Ni.

means repulsion. We can see that in all these cases there is attraction. However, the on-top site has the biggest B.E.. From the Ni-P overlap populations we see that there forms a strong P–Ni bond at the on-top site, two less strong bonds at the twofold site, and three still weaker bonds at the threefold site. According to these two criteria, energy and overlap population, we conclude that PF_3 likes to bind to the on-top site.

Let us discuss in some detail at the bonding between PF_3 and $Ni(111)$ surface in the on-top site. Figure 2 shows (a) the DOS curves of the bare Ni surface along with some important frontier orbitals of PF_3, and (b) the whole system after chemisorption. Comparing the orbitals around − 18 to − 20 eV in Figs. 2(a) and 2(b), we can see that they do not move much. This indicates very little interaction with the surface. However, the n orbital, originating at − 13.4 eV, now is pushed down to − 15 to − 15.4 eV. This P lone pair clearly interacts strongly with the surface. The calculated position of the n orbital, 6.3 eV below the Fermi level, is in good agreement with the He II UPS spectrum of PF_3 on $Ni(111)$.[9(c)] The n level is assigned in the experiment to a band of 6.5 eV below ϵ_f.

Where do the degenerate π^*'s go? One cannot see that very well in this graph, but if we project the π^*'s and magnify them, we can see from Fig. 3 that most of their election density has been pushed up above the energy range of this diagram (from the integration curve). However, there is some π^* density in the metal d and s, p band, and 10% of these orbitals come below the Fermi energy. Even though the π^*'s are at an energy that is so far away from the metal d states, they still have an interaction with the surface. PF_3 remains a π acceptor, at least to some extent.

Now which orbitals on the surface are responsible for all these interactions? As can be seen in the COOP plot in Fig. 4, the biggest peak is at − 15.2 eV, which corresponds to the n
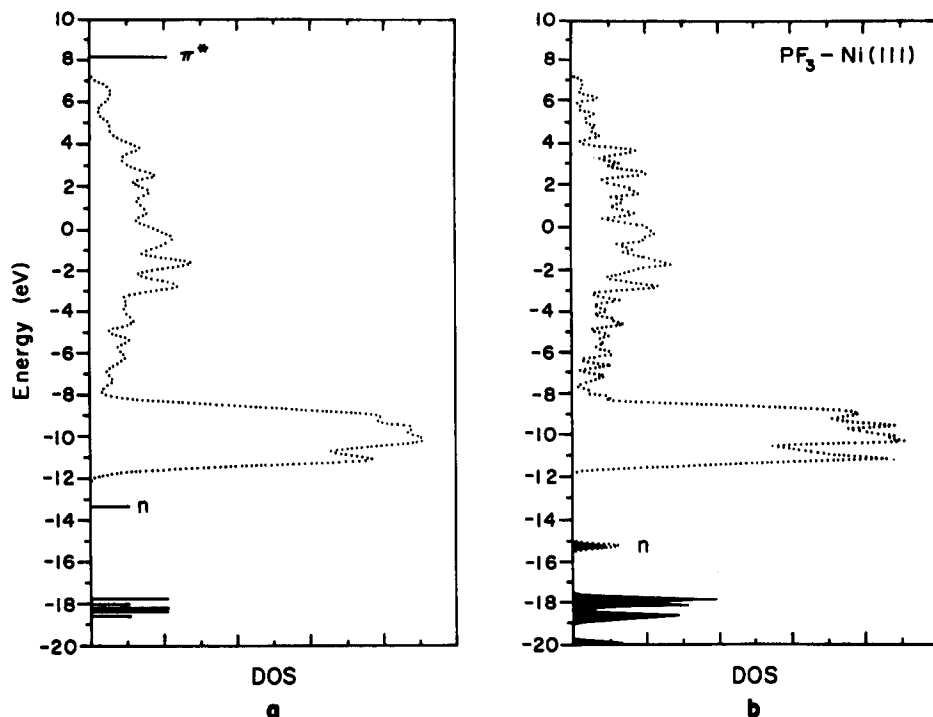
FIG. 2. (a) Total DOS of the Ni(111) surface (dotted line) and the energy levels of the PF₃ molecule (sticks). (b) DOS upon chemisorption of PF₃ on the Ni(111) surface, with projected PF₃ (shaded).

orbital [compare the DOS curve in Fig. 2(b)].

The Ni–P overlap position population is 0.73. We can approach an analysis of this total Ni–P overlap population in two ways. First we can look at the orbital by orbital contributions to this. For instance, from the Ni side, we have the following contributions: $Ni(s + p_z)$–P = 0.63; $Ni(d_{z^2})$–P = 0.06; $Ni(d_{xz} + d_{yz})$–P = 0.07. This clearly indicates a major role for the metal s and p_z orbitals, and a dominant σ interaction. The latter conclusion is also supported by a partitioning on the P side: $Ni–P(s + p_z)$ = 0.64; $Ni–P(p_x + p_y)$ = 0.09. The metal s, p_z and d_{z^2} orbitals thus

contribute most to σ bonding, through interactions of type **5** with the PF₃ n orbital. This is confirmed by resonances in the relevant contributions to the DOS, not shown here.
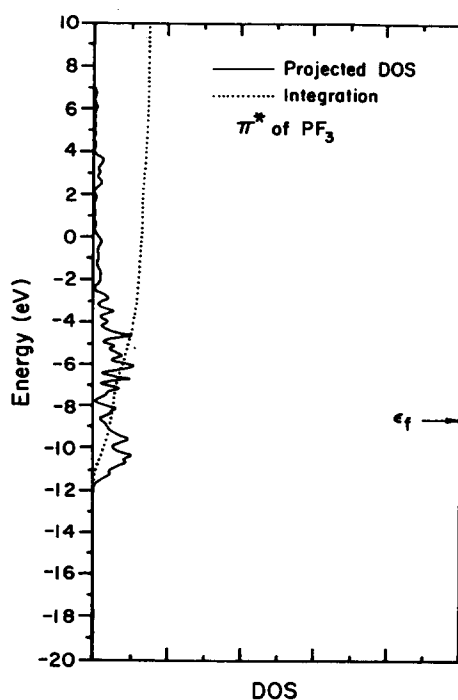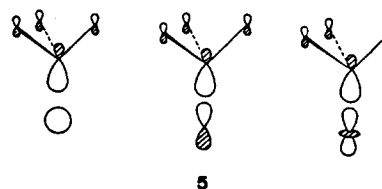

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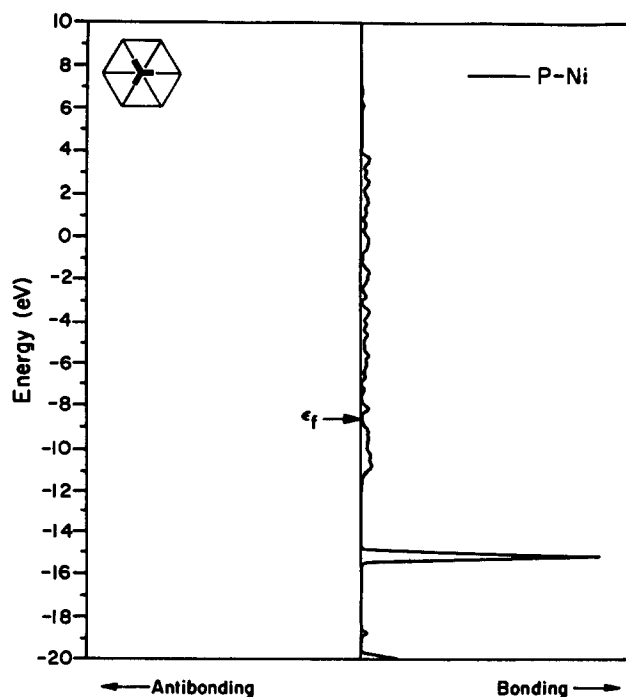FIG. 3. Magnified (50×) projected DOS of the π^* orbitals of PF₃.

FIG. 4. The Ni–P COOP curve for the chemisorption of PF₃ in the on-top site.

Another way to approach an analysis of the bonding is to look at contributions to the total overlap population by energy range. This can be done by repeating the calculations for different electron counts or Fermi levels. For instance, if ϵ_f is chosen at -16 eV, below the n band of Fig. 2(a), one gets a contribution to the overlap population from all the lower levels of 0.32. (The total Ni–P overlap population is 0.73.) Occupying the n band, which is mainly responsible for σ bonding, adds 0.27. Completing the filling through the d band, which presumably picks up the π bonding, adds the final 0.14. The n interaction is almost two times larger than the π^* interaction. The orbitals involved in π bonding are shown in 6.


6
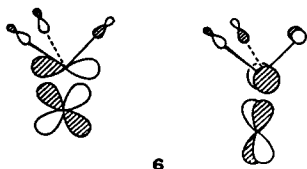
Further insight into the bonding mechanism is provided by analyzing the charge distributions. A schematic diagram to illustrate the bonding of the system is shown in 7; the numbers are net charges, not electron densities. The total charge on PF₃, when it is bound to the surface, is $+0.34$. PF₃ and the metal are both neutral when they are separated. Therefore, electrons are transferred from PF₃ to the metal surface; i.e., PF₃ acts as a donor. If we look further into the matter, we find that the n orbital actually loses 0.53 electrons, and the π^*'s gain 0.19 electrons. This is additional evidence that PF₃ is a σ donor and a π acceptor. However, the on-top Ni does not gain electron density at all. In fact, it loses electrons. The other Ni atoms on the surface, which do not bond directly to P, retain their charges, which are still -0.09. Where do the electrons go?

7
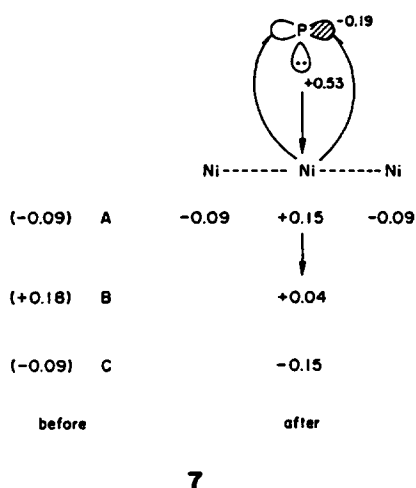
Actually, the inner layers in the bulk act as a sink for the donated electrons. The metal slab is able to shift electron density between the bulk and the surface layer; the charge transfer has both a localized and a delocalized component.

Besides the metal-phosphorus bonding, there are other bonding interactions going on in the system. First consider the bonding of Ni with F of PF₃. It was suggested[28] that PF₃ might prefer the on-top site, with F atoms orienting in the

direction of neighboring Ni atoms, because of secondary F–Ni bonding effects. From our calculation, the F–Ni overlap populations are extremely small on all sites, and they are all slightly antibonding. So F–Ni bonding interactions are unlikely. However, this kind of interaction still has a slight effect on the system, depending on the geometry. Looking at the binding energy, adsorption at the threefold-1 site is less favorable than anywhere else, but the Ni–F overlap population in this site is the most antibonding among all sites. The reason for this is that the fluorine atoms are pointing directly toward the Ni atoms. Also, the distances between Ni and F in threefold-1 site are the shortest of all. The interactions responsible for the antibonding are sketched in 8, and the COOP curve for the various interactions is illustrated in Fig. 5.

8
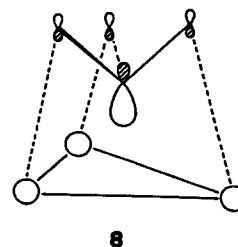
One can see from Table II that the overlap population between the Ni atom which is bonded to the phosphorus and the other surface Ni has decreased, while other Ni–Ni overlaps remain the same. Hence the P–Ni bond forms at the expense of weakening the Ni–Ni bonds.

We mentioned at the beginning of this section that the rotational barrier for the PF₃ group should be small. It is calculated, in fact, to be 0.05 eV in the on-top site, 0.24 eV in
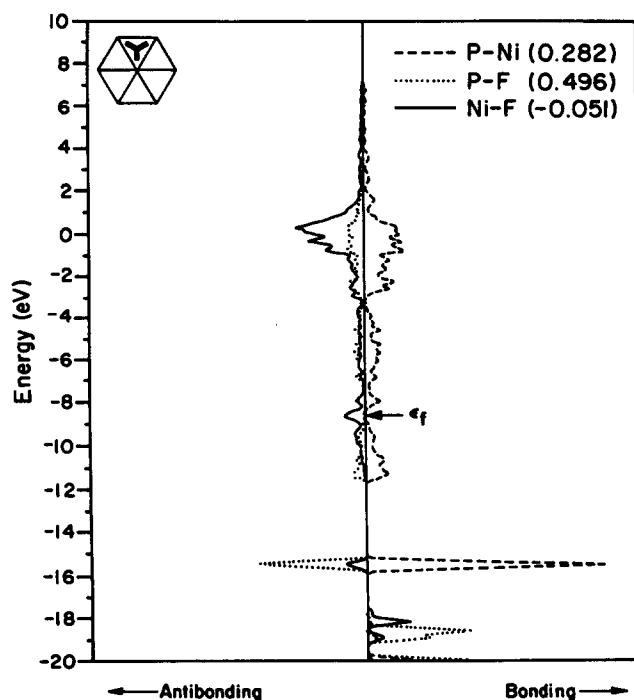

FIG. 5. The P–F, P–Ni, Ni–F COOP curves for the chemisorption of PF₃ in the threefold site. The numbers in the legend indicate the total overlap population at the Fermi level.

the twofold site. In each case the orientation shown in **4** being favored. Also, as indicated earlier, the Ni–P bond length is kept constant (2.0 Å).

One might have thought that Ni–P distances would change with bonding mode, but an examination of available discrete molecular structures does not support this. For instance in a $(PCy_2)(CO)_2Re(\mu\text{-}PCy_2)_2Ir(PCy_2)(CO)_2$ (Cy = Cyclohexyl) complex,[13(b)] an Ir–P bridging distance is actually shorter than a corresponding terminal one.

To conclude this section: PF₃ is primarily a σ donor, i.e., upon chemisorption, electrons shift from the PF₃ lone pair to the metal. At the same time, the π orbitals accept some electrons from the surface. The on-top site is the most favorable one for PF₃ chemisorption.

EFFECT OF PHOSPHORUS 3d ORBITALS

To probe the role of phosphorus 3d orbitals, we repeated our calculations including a set of such orbitals, with exponent = 1.4, and Coulomb integral = − 1.0 eV.[26,29] We think these are reasonable guesses for simulating moderate 3d orbitals interactions. Table III shows the results. On the molecular level, the mixing of d orbitals with the fluorines brings down the energy level of the π* orbitals (from ∼ + 8 → ∼ − 6 eV), thus making them better acceptors relative to the surface. The LUMO of PF₃ actually contains substantial P–F σ* character in addition to some P 3d character.[23,24] To be specific, now the π* contains 87% P (53% of which is p and 47% d) and 13% F character. This orbital is well hybridized toward the metal. Donation into it should weaken the P–F bond. In fact, the P–F overlap population in PF₃ on the surface is smaller than in the molecular case. The Ni–P overlap populations have also increased relative to those without d orbitals.

TABLE III. Effect of phosphorus d orbitals on the chemisorption of PF₃ on Ni(111) surface.

	on-top	2-fold	3-fold
Energies:			
ϵ_f [a]	− 8.56	− 8.56	− 8.60
B.E.[b]	3.82	4.28	4.62
Overlap populations:			
Ni–P	0.92	0.62	0.51
P–F[c]	0.53	0.53	0.52
Ni–Ni[d]	0.10	0.08	0.08
Ni–Ni[e]	0.05	0.04	0.05
Ni$_b$–Ni$_b$ [f]	0.11	0.11	0.11
Ni$_b$–Ni$_s$ [g]	0.10	0.10	0.10

[a] Fermi energy in eV.
[b] Binding energy = [E(slab) + E(PF₃)] − E(system), in eV.
[c] Molecular overlap population for P–F (with d orbitals) = 0.55 in free PF₃.
[d] Overlap population between the surface Ni atoms.
[e] Overlap population between the bonded Ni and the other surface Ni atoms.
[f] Ni$_b$ = bulk Ni.
[g] Ni$_s$ = surface Ni.

If we look at the binding energies, it will be seen that the site preferences of the above discussion are reversed. With d orbitals on phosphorus the threefold site is favored, which is not in agreement with the experimental observations. It seems that this choice of P 3d functions gives the adsorbate too much π-accepting power, a quality that would make it favor the threefold site. For instance this is what drives adsorbates such as CH,[30] CCH₃,[31] and, as we will see, PF into the threefold site.

ADSORBED PF₂

Our procedure for analyzing PF₂ follows the lines of the PF₃ analysis. Three adsorption sites, onefold on-top, twofold bridging, threefold capping, are shown in **9**.

9
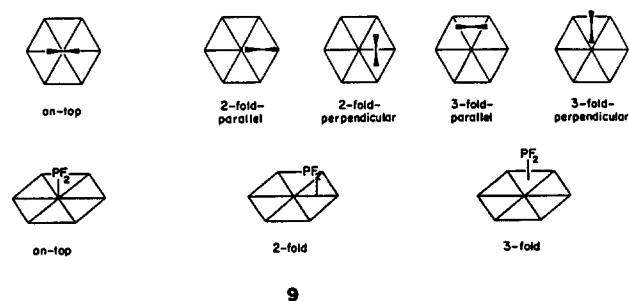
As in the PF₃ case, in each site a range of rotations around the surface-P axis may be studied. However, for the on-top site the rotational barrier is sixfold and thus unlikely to be large. We will report only one conformation for the on-top site, and two conformations for the other two sites.

The P–Ni and P–F bond distances are taken as 2.0 and 1.57 Å, respectively. The F–P–F bond angle of is 110°.[27] The PF₂ radical has 12 orbitals. The two most important ones are the HOMO (π*) and the next HOMO (σ) (see **10**). The energy of σ is at − 14.43 eV. The singly occupied π* orbital lies at − 11.3 eV. These two orbitals are the two lone pairs of a phosphido group, PR_2^-. In neutral PF₂ they are occupied by three electrons.
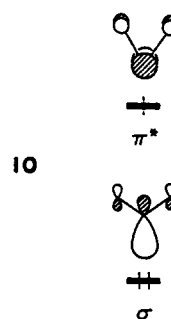

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Table IV shows a selection of the computed binding indicators for all the different sites. Let us see if we can pick out the most favorable site for PF₂ from the data. The binding energies of the twofold-perpendicular and threefold-perpendicular sites are the lowest and they are quite similar. The difference is 0.28 eV, a relatively small number. If one looks at the P–Ni overlap populations, there are two strong P–Ni bonds in the twofold-perpendicular site, and three weaker bonds in the threefold-perpendicular site. The sum of the

TABLE IV. Consequences of approaching PF_2 to Ni(111) surface in different orientations.

	on-top	2-fold-parallel	2-fold-perpendicular	3-fold-parallel	3-fold-perpendicular
Energies:					
ϵ_f [a]	− 8.56	− 8.56	− 8.54	− 8.56	− 8.54
B.E.[b]	5.82	6.04	6.58	6.80	5.99
C.B.E.[c]	2.36	2.58	3.12	3.34	2.53
Overlap populations:					
Ni–P	0.73	0.40	0.70	0.45	0.48
P–F[d]	0.43	0.47	0.45	0.48	0.47
Ni–Ni[e]	0.10	0.07	0.08	0.07	0.07
Ni–Ni[f]	0.05	0.03	0.04	0.04	0.04
Ni_b–Ni_b [g]	0.11	0.11	0.11	0.11	0.11
Ni_b–Ni_s [h]	0.10	0.10	0.10	0.10	0.10

[a] Fermi energy in eV.
[b] Binding energy = $[E(\text{slab}) + E(PF_2)] − E(\text{system})$, in eV.
[c] Covalent binding energy in eV (see text for definition).
[d] Molecular overlap population for P–F = 0.45 in free PF_2.
[e] Overlap population between the surface Ni atoms.
[f] Overlap population between the bonded Ni and the other surface Ni atoms.
[g] Ni_b = bulk Ni.
[h] Ni_s = surface Ni.

Ni–P overlap populations in the twofold-perpendicular site is about the same as in the threefold-perpendicular one. We do not see much of a difference between the two. Experiment prefers the twofold-perpendicular site.

Let us look at how PF_2 binds to the metal surface at the twofold-perpendicular site. Figure 6 shows (a) the DOS curves of the bare Ni surface along with some important frontier orbitals of PF_2, and (b) the whole system after

chemisorption. σ is pushed down from − 14.5 to − 16.3 eV. The π^* has also been pushed from − 11.3 to − 13 to − 14 eV. The interactions here are quite similar to those of PF_3. σ acts as an electron donor and π^* as an acceptor. In contrast to PF_3, however, the π interactions are important, obviously a consequence of the low-lying π^* acceptor level.

Why does PF_2 prefer the twofold-perpendicular site 11 to the twofold-parallel site 12? 11 has a substantially lower energy and a higher P–Ni overlap population.
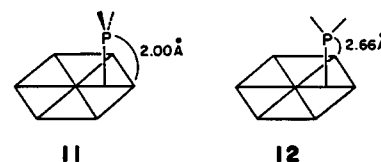
The difference in energy (0.54 eV) is the rotation barrier between these two conformations. Let us look at the COOP curves (Fig. 7) for these two orientations. For the twofold-perpendicular site, the σ and π^* overlap populations are ~0.25 and 0.28, respectively. For the twofold-parallel site, they are ~0.23 and 0.07, respectively. One can conclude then in twofold-perpendicular site, the interaction is half σ and half π, while in twofold-parallel site only σ remains, the π interaction being much diminished.

The large rotational barrier and the greater Ni–P overlap populations in the "perpendicular" conformation derive from the same source. In the perpendicular geometry, the π^* is well oriented for bonding interactions of the type shown in 13a or 13b. These are absent in the parallel conformation. The corresponding overlaps shown in 13c are smaller, operating over longer distances. The situation is very similar to that of CH_2 on metal surfaces, analyzed earlier[30] by us. Also
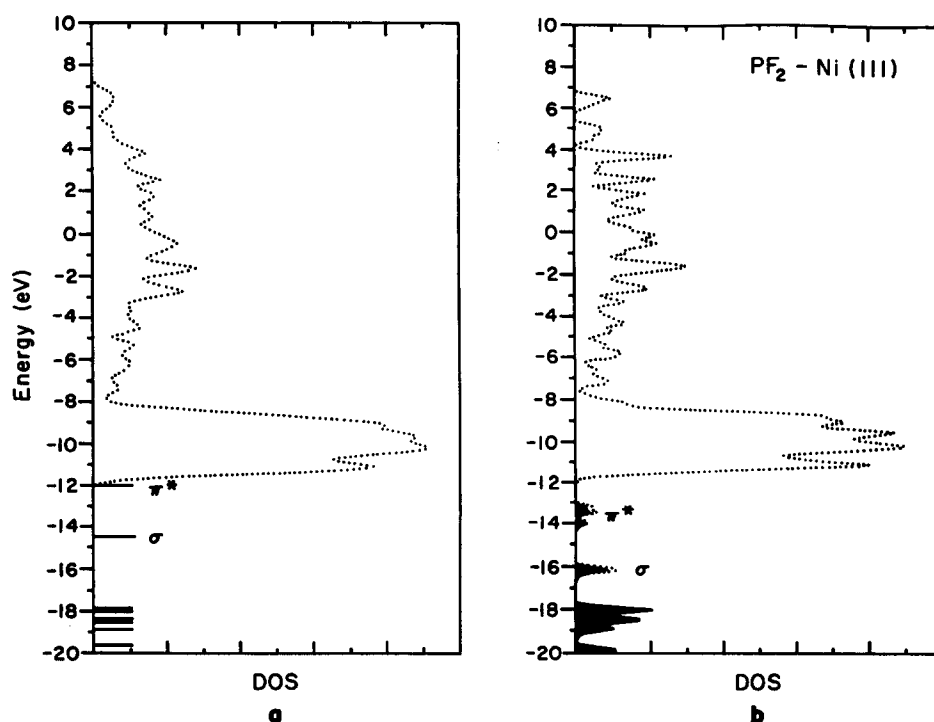
FIG. 6. (a) Total DOS of the Ni(111) surface (dotted line) and the energy levels of the PF_2 molecule (sticks). (b) DOS upon chemisorption of PF_2 on the Ni(111) surface, with projected PF_2 (shaded).
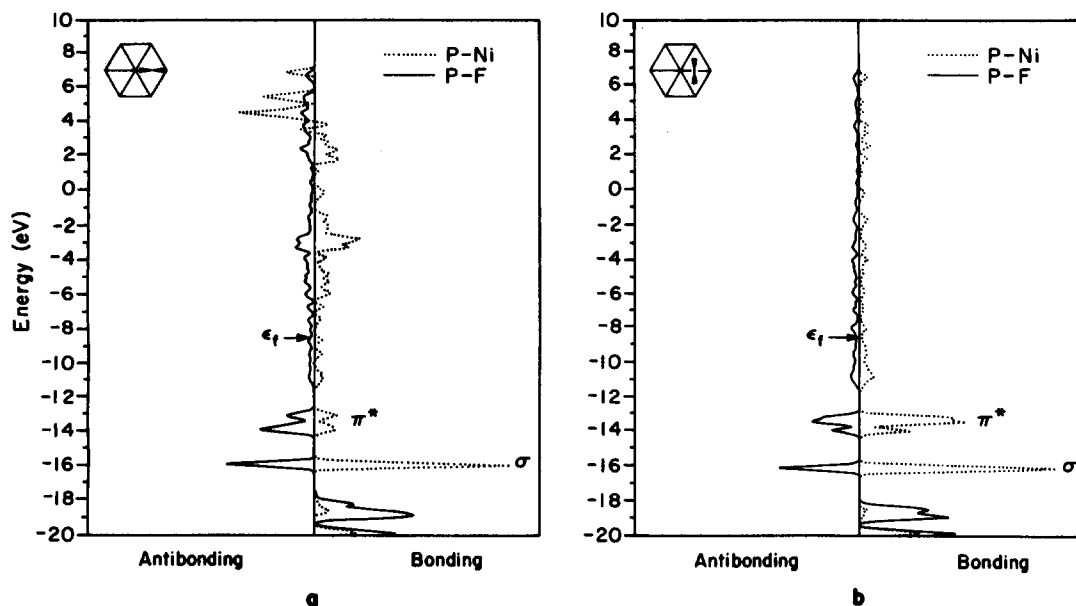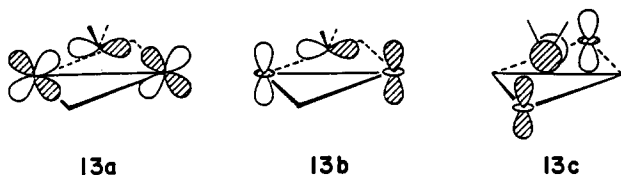
FIG. 7. (a) the P–Ni, P–F COOP's for the PF_2 twofold-parallel site. (b) The P–Ni, P–F COOP's for the PF_2 twofold-perpendicular site.

in discrete organometallic compounds one never sees a parallel-type bridging PR_2 ligand, only a perpendicular one.

In the beginning of this section, we mentioned that the rotational barrier for the PF_2 group in the on-top site should be small. It is calculated, in fact, to be 0.10 eV, the orientation shown in 9 being favored.

We need to discuss further the binding energy. Assuming a neutral PF_2, as we have, there is a singly occupied orbital below the Fermi energy. It acts as a hole. As the adsorbates approach the surface, electrons will fill up this hole (this is just a way of thinking, for we know these fragments are formed by reactions on the surface). We refer to this as the ionic or electron transfer component of the interaction.[30] To see the actual covalent contribution, we have to subtract out the ionic or electron transfer part of the interaction. The procedure is as follows: we define the ionic part of the energy as the difference between the Fermi energy and the energy of that singly occupied orbital. Then the covalent part is equal to the difference of the binding energy and the ionic part. Table IV gives the value of the covalent binding energy (C.B.E.) at all sites.

If we compare the C.B.E. for PF_2 with the B.E. of PF_3 case, we see that their values are very similar. Therefore, we can conclude that the loss of a P–F bond does not increase the covalent binding between P and Ni. Or, to put it another way, a PF_2^- (one electron transferred, now principally a donor) binds to this surface much as PF_3 does.

If we put d orbitals on P, as discussed earlier for PF_3, we once again get similar binding energies for the twofold-perpendicular and threefold-perpendicular sites. All the Ni–P and P–F overlap populations are increased, but little else

changes. There is more π donation from the surface to PF_2, as expected.

An interesting final comment follows from the nearly equal energy of the twofold-perpendicular and threefold-perpendicular site of PF_2. We calculate only a 0.20 eV energy difference between these sites. If these theoretical calculations are correct, then there should exist an easy migration route on this surface, a kind of shuttling around a Ni atom, as illustrated from the top in 14.
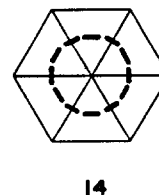
ADSORPTION OF PF

This analysis is similar to the cases described above. From the experimental data,[17] a single intense F^+ central ESDIAD pattern is observed. This is likely to be generated by a fluorine atom which is directed normal to the surface. We will assume this in our calculations. There is then only one orientation on each site considered, and 15 displays the relevant geometries.
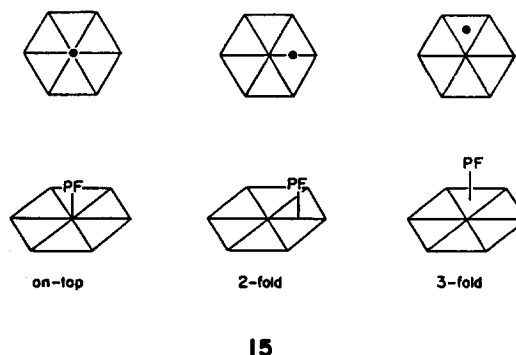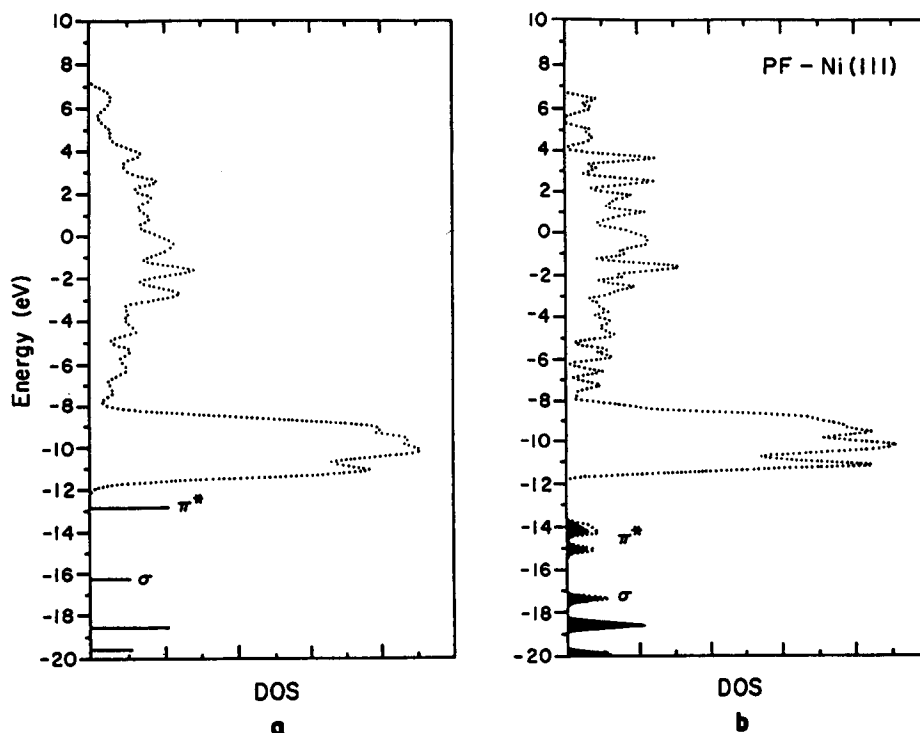
FIG. 8. (a) Total DOS of the Ni(111) surface (dotted line) and the energy levels of the PF molecule (sticks). (b) DOS upon chemisorption of PF on the Ni(111) surface, with projected PF states (shaded).

Table V summarizes the computational results for these three sites. The P–Ni and P–F bond lengths are kept at 2.0 and 1.57 Å, respectively.

The PF radical has eight molecular orbitals. **16** shows the molecular orbitals of the partially occupied HOMO and the next HOMO.
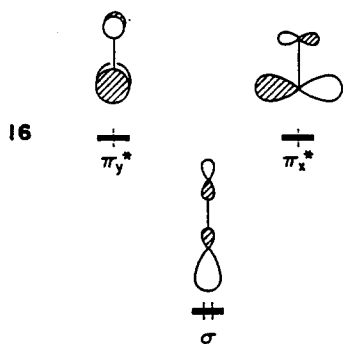
In increasing order of energy, one finds a filled σ molecular orbital lying at -16.2 eV and a pair of half-filled degenerate π orbitals at -12.95 eV. Chemisorption of CH[30] on various metals and CCH$_3$[31] on Pt(111) were discussed before by our group as well as by others. Both CCH$_3$ and CH have one electron housed in their degenerate π orbitals. The interactions of both systems were governed by these π orbitals. In PF we see similar orbitals, and one more electron. Since, the π's of PF lie closer to the metal d states and they are half filled, we expect that the interaction between PF and the surface will be mainly π type.

Judging from the binding energy reported in Table V, the threefold site should be preferred. The P–Ni overlap populations in all sites are very similar, but there are three of them in the threefold site. In Table V, we also give the values of the covalent binding energy (C.B.E.) defined above. This time, since there are two unfilled orbitals, the ionic part of the binding energy should be equal to the energy difference

between the top of the bare Ni band and the π orbital hole, multiplied by 2 (for 2 electrons). This amounts to 8.72 eV. After subtracting out the ionic interaction, there is essentially no covalent binding at the on-top site. We have already discussed that on-top site favors σ interaction. But in this case the π interaction dominates, and it is optimal in the threefold site. Experiment also favors the threefold site for PF adsorption.

Figure 8 shows (a) the DOS curve of the bare Ni surface along with some frontier orbitals of PF, and (b) the whole system after chemisorption at the threefold site.

TABLE V. Consequences of approaching PF to Ni(111) surface in different orientations.

	on-top	2-fold	3-fold
Energies:			
ϵ_f [a]	-8.56	-8.54	-8.54
B.E.[b]	8.46	10.73	11.52
C.B.E.[c]	0.00	2.27	3.06
Overlap populations:			
Ni–P	0.65	0.65	0.62
P–F[d]	0.37	0.42	0.42
Ni–Ni[e]	0.10	0.08	0.07
Ni–Ni[f]	0.05	0.03	0.03
Electron occupations:			
σ	1.67	1.61	1.59
π^*	3.41	3.00	2.91

[a] Fermi energy in eV.
[b] Binding energy $= [E(\text{slab}) + E(\text{PF})] - E(\text{system})$, in eV.
[c] Covalent binding energy in eV.
[d] Molecular overlap population for P–F $= 0.51$ in free PF.
[e] Overlap population between the surface Ni atoms.
[f] Overlap population between the bonded Ni and the other surface Ni atoms.

TABLE VI. Extended Hückel parameters.

Atom	Orbital	H_{ii} (eV)	ζ_1	ζ_2	c_1 [a]	c_2 [a]
Ni	$4s$	-7.8	2.100			
	$4p$	-3.7	2.100			
	$3d$	-9.9	5.750	2.00	0.5683	0.6292
P	$3s$	-18.6	1.750			
	$3p$	-14.0	1.300			
	$3d$	-1.0	1.400			
F	$2s$	-40.0	2.425			
	$2p$	-18.1	2.425			

[a] Coefficients used in the double-ζ expansion of the d orbitals.

Comparing these two graphs, the σ orbital here is pushed down to -17.4 from -16.2 eV. π's are pushed down from -12.93 to -13.5 to -15.5 eV. The electron occupations of σ and π before the interaction are both 2.00. But now they are 1.59 and 2.90, respectively. σ has donated some electrons to the surface while the π's have gained some electrons from the surface. Overall, PF has a net charge of -0.49.

Detailed analysis of the orbital interactions reveals that there is significantly better π bonding in the threefold site. The most important interactions are those with local symmetry-adapted combinations of d_{z^2} and $d_{xz,yz}$ of type 17.
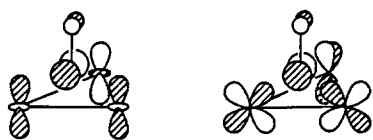
17

As we have discussed before, adding d orbitals on P will enhance the π interaction, thus favoring the threefold site. This was done; the computational results with d functions are very similar with those without the d orbitals, since π interaction dominates here.

ACKNOWLEDGMENTS

APPENDIX

The tight-binding extended Hückel method[32,33] was used for all the calculations. Parameters used are listed in Table VI. Sets of 16 k points[34] were used on the bare nickel surface calculation. Sets of 10 or 7 k points[34] set were used in the system with the adsorbates, depending on the geometry. The d(Ni–P) and d(P–F) were kept at 2.0 and 1.57 Å, respectively, in all cases.

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