

**TOPOLOGICAL STUDY OF THE CHEMISORPTION OF N<sub>2</sub> ON (112) STEPPED SURFACES OF Pt AND Ir**

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Interaction of N<sub>2</sub> molecule with stepped (112) Ir and Pt surfaces has been studied by a quantum chemical topological method. The adsorption of N<sub>2</sub> takes place preferentially in top bound configurations. The reactivity of the N<sub>2</sub> molecule chemisorbed on the studied (112) surfaces of Pt can be expected to be increased for electrophilic reagents, while chemisorption of N<sub>2</sub> molecules on the studied Ir surfaces apparently does not affect their reactivity.

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The N<sub>2</sub> molecule is the most inert of all the known biatomic molecules. Its unusual stability is a result of the electronic structure of N<sub>2</sub> (ref.<sup>1</sup>), leading to: (i) high energy of the N≡N triple bond (946 kJ mol<sup>-1</sup>), (ii) relatively small internuclear distance (0.110 nm), (iii) high vibration energy value (2.331 cm<sup>-1</sup> in the Raman spectrum, see ref.<sup>2</sup>), (iv) extremely high energy for reduction of the triple bond to a double bond (524 kJ mol<sup>-1</sup>), (v) extremely high ionization potential value (1 514 kJ mol<sup>-1</sup>).

Consequently, molecular nitrogen is only slightly dissociated to the free atoms at room temperature and at temperatures common for chemical reactions (and even at 3 000°C). Thus, the chemical conversions of molecular nitrogen require very high reaction temperatures in the presence of a catalyst. These factors have led to a search for substances capable of catalyzing the reactions of molecular nitrogen and to investigation of the mechanisms of these catalytic processes.

This work summarizes the results obtained in a study of the dissociative and non-dissociative chemisorption of N<sub>2</sub> molecules on stepped (112) surfaces of selected fcc metals, Pt and Ir.

The (112) plane was selected intentionally as it has been found experimentally and theoretically (see, e.g. refs<sup>3-10</sup>) that steps and defects in the surface are important for activation of chemisorbed molecules on fcc transition metals. The (112) plane is the plane with the lowest Miller indices that still contains steps.

The metals Pt and Ir were selected on the basis of the calculations in ref.<sup>11</sup> where it was found that the atoms on the surface plane of Pt have the most negative charge of all the fcc transition metals, the atoms on the Ir surface plane having the most

positive charge. Consequently, different result can be expected in the chemisorption of molecules on these metals.

Experiments have actually demonstrated that the mechanisms of the chemisorption of N<sub>2</sub> molecules on the surfaces of various metals do, in fact, differ — they depend on the magnitude of the charge on the surface, crystallographic structure, chemisorption temperature and other factors.

It has been found experimentally, e.g. refs<sup>5,12,13</sup>, that molecular nitrogen is adsorbed on low-index planes of the Pt surface in positions above the individual surface Pt atoms<sup>5</sup>, or in bridging positions<sup>13</sup>. Less attention has been paid to the study of the chemisorption of molecular N<sub>2</sub> on stepped surfaces. For example, ref.<sup>10</sup> summarizes the results of the study of the chemisorption of N<sub>2</sub> on the Pt-9(111) × (111) plane. It has been found that molecular adsorption predominates at low temperatures, changing to dissociative adsorption on “active sites” at temperatures above room temperature. However, nondissociative adsorption still predominates as a result of the low contents of “active sites” on the metal surface. The nitrogen molecules are also adsorbed linearly on iridium surfaces (refs<sup>14–17</sup>).

Recently, one of us developed a quantum-chemical topological method<sup>18</sup> with a very simplified computation scheme as compared to the other MO methods which, however, permits very satisfactory qualitative description of the system including dozens of atoms and hundreds of valence electrons in the calculation. This method has been successfully applied to the study of pure metal surfaces<sup>19</sup> and has recently been employed to study the interaction of molecules with the metal surface<sup>8,20–27</sup>. This method was employed in the calculations forming the basis for this work.

## THEORETICAL

### *Method*

The method used has been described in the preceding paper<sup>8</sup>. This is the reason why computation details are not presented here. The method includes a single matrix diagonalization, and thus calculations can be carried out including 500 or more valence electrons without unduly prolonging the computation time.

The following approximations were adopted in the above method: (i) the Born–Oppenheimer approximation, (ii) the valence electron approximation, (iii) selection of a base of hybrid orbitals corresponding to the given structural type, (iv) neglecting of the correlation energy, (v) complete neglecting of electron repulsion, (vi) neglecting of the resonance integral between atoms not connected by a chemical bond, (vii) neglecting of overlap integrals.

These approximations permit us to obtain all the observable quantities through diagonalization of the matrices of the Coulomb integral  $\alpha$  and the resonance integral  $\beta$ .

The program obtains the  $\alpha$  values from preprogrammed equations for the correlation between the electronegativities and Slater effective charges. Table I lists the values used in the correlation.

The corresponding values of the resonance integrals between the equivalent orbitals lying on the line connecting the atomic nuclei are  $-172$ ,  $-132$ ,  $-74$ ,  $-54$ , and  $-104$  for Pt—Pt, Ir—Ir, Pt—N, Ir—N and the adsorbed N—N molecule, respectively.

For treating resonance integrals of a metal-adsorbate in bridge and hollow positions it was assumed that the corresponding bond lengths approach those for top positions. The corresponding metal — N energy reduction was obtained using a Morse function. The values of the  $\beta$  integrals between the equivalent orbitals of the neighbouring atoms are  $-14$  and  $-12$  kJ mol<sup>-1</sup> for the Pt—N and Ir—N bonds, respectively.

### Model System

This work summarizes the results obtained for the chemisorption of molecular N<sub>2</sub> on stepped (112) crystal faces of the transition plane-centred metals Ir and Pt (Fig. 1). It can be seen that the (112) plane under study is formed of terraces represented by (11) planes and the fronts represented by (100) planes (hatched in the figure). Consequently, the (112) plane can be considered to be a plane consisting of (111) and (100) planes. The atoms shown as full squares designate the basic structural unit employed in the calculations, consisting of 27 metal atoms (see Fig. 2b).

Transition from the atomic clusters to the infinite metal crystal was accomplished through selection of periodic boundary conditions, where the atoms on the left-hand side of the basic structural unit were connected to the atoms on the right-hand side by a formal chemical bond. The atoms at the front were connected to the atoms at the back of the basic structural unit and bonds were formed between suitably oriented equivalent orbitals so that the required step was formed.

Uniform hybridization  $sp^3d^5f^3$  was assumed for the orbitals of the atoms of the metals studied, i.e. twelve equivalent orbitals directed to twelve neighbouring orbitals of atoms in the face centred cubic lattice. This hybridization was also considered for

TABLE I  
Negative values of the Mulliken orbital electronegativities kJ mol<sup>-1</sup> for the elements studied

Element	Orbital			
	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>
Ir	-655	-251	-872	0
Pt	-382	-125	-886	0
N	-1965	-781	-130	0

atoms lying on the metal surface, where their lone orbitals lie in the direction of crystal growth<sup>27</sup>. Under these conditions, the (112) plane can be depicted in the manner shown in Fig. 3.

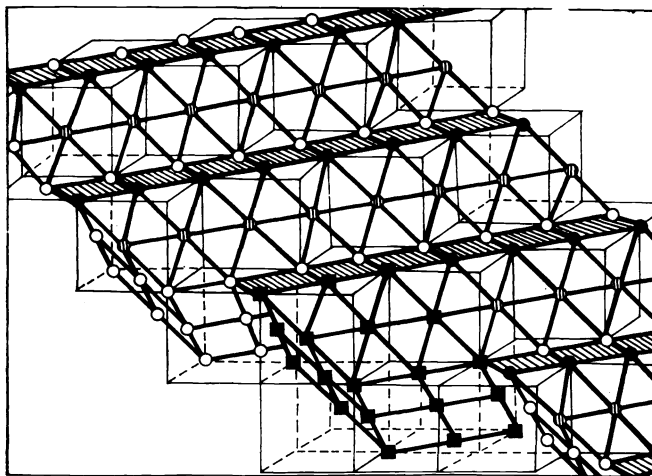


FIG. 1

The (112) crystal face. The circles designate surface atoms and atoms in the two subsurface planes with lone orbitals. The squares designate the basic structural units used in the calculation. The hatched area corresponds to the front of step (100) and the white areas are the (11) terraces

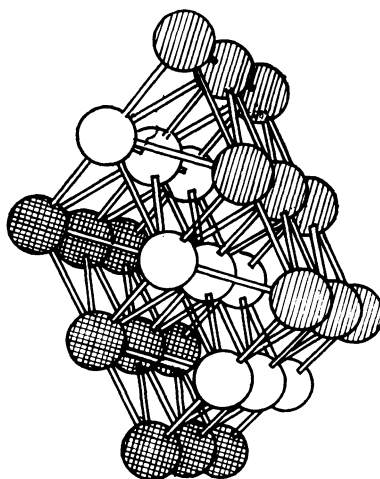


FIG. 2

The basic structural unit used in the calculation. The circles designate the individual subplanes parallel with the terraces

Atoms with lone orbitals lie in the surface and subsurface (112) planes. The lone orbitals extend above the surface in three ways and the intercepts correspond to the crystal growth positions. These intercepts correspond to sites for multiple adsorption of the chemisorbed gas molecules.

There are three types of capture of  $N_2$  molecules on the studied surface, involving direct interaction with the metal atom orbitals. Considering also the orientation of the  $N_2$  molecules, which are roughly perpendicular to the (A) terrace or to the edge of the (B) step, ten types of capture of  $N_2$  molecules can be distinguished as shown in Fig. 4. The true A or B orientations were directed in the axes of a set of appropriate equivalent orbitals. This was done because bonds in this topological method are defined by localizations of equivalent orbitals rather than by geometrical relations. A and B orientations differ because, in contrast to conventional topological methods, this approach considers interaction between all the equivalent orbitals of neighbouring atoms, as mentioned in the theoretical part of this work. Symbol I designates capture of a  $N_2$  molecule at a five-fold site, symbols II and III, three-fold sites and two-fold sites, respectively. Symbols IV, V and VI correspond to the capture on single atoms of three surface planes of the (112) crystal cross-section studied.

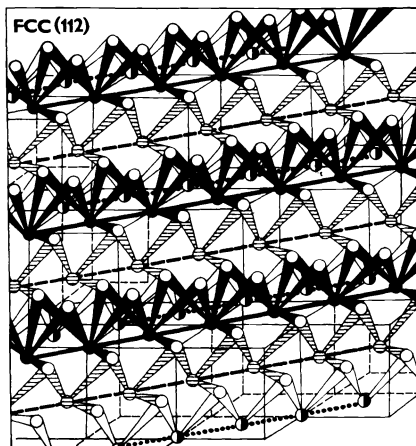


FIG. 3  
The direction of equivalent orbitals on the surface of the (112) crystal face

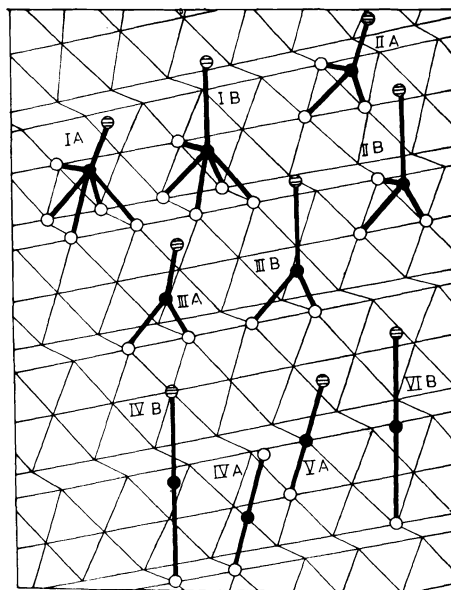


FIG. 4  
Considered types of nondissociative chemisorption of  $N_2$  on the surface of the (112) crystal face

In addition to the nondissociative chemisorption of molecular N<sub>2</sub>, dissociative chemisorption was also studied. The studied types of capture of N<sub>2</sub> molecules are shown in Fig. 5, where the designation of the individual types of molecular capture is as above.

## RESULTS AND DISCUSSION

### *Comparison of Clean Pt and Ir Surfaces*

The basic structural unit used in the calculation consisted of 27 metal atoms lying in nine crystal planes. The charge densities on the atoms of the individual planes of the (112) surface and the bond orders between the atoms of these planes are given in Table II for the metals studied.

As mentioned in the introductory part the charge densities on the (112) crystal faces of the individual metals have completely different values. It can be seen from Table II that the atoms of the surface plane of Pt have a negative charge, those of the surface plane of Ir have a positive charge.

The strong negative charge localized on the surface Pt atoms is greatly compensated by the positive charge of the atoms of the first subsurface layer, where further sites

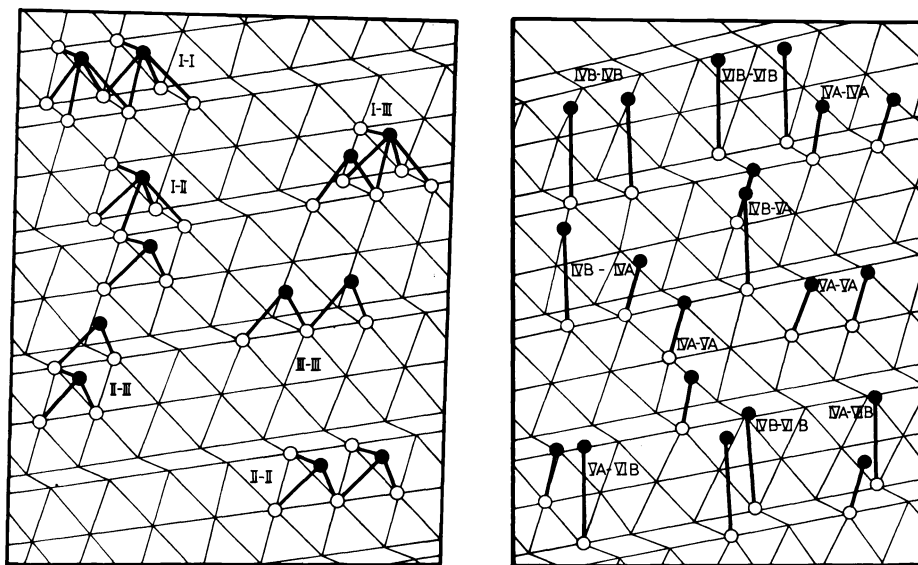


FIG. 5

Considered types of dissociative chemisorption of N<sub>2</sub> on the surface of the (112) crystal face: *a* captures on *n*-fold hollow centers, *b* captures on a top centers

with a marked positive charge lie in the centre of the crystal. An electrical double layer occurs between the surface and the first subsurface planes, which is not found for the other metals studied. Considering the overall charge on the first three planes of the Pt surface participating in chemisorption of the  $N_2$  molecule, the studied Pt surface has a negative total charge.

In contrast, the marked positive charge of the surface plane of Ir is not sufficiently compensated by the negative charge on the second subsurface plane. The three surface planes of the studied (112) crystal faces of the Ir surface thus have a positive total charge.

The charge densities localized on the atoms of the individual planes of the other low-index planes of Pt are listed in Table III. The considerably more uniform charge distribution on the smooth planes than on the stepped plane is evident. This fact

TABLE II

Charge densities  $q$  and bond orders  $p$  for the individual planes of the (112) surface of the metals studied

Plane	$q$		$p$	
	Ir	Pt	Ir	Pt
1	+0.22	-0.56	1.36	1.22
2	+0.07	+0.22	0.85	0.92
3	-0.16	+0.13	0.78	0.73
4	-0.12	+0.11	0.67	0.66
5	+0.03	+0.22	0.75	0.65
6	-0.12	+0.11	0.67	0.66
7	-0.16	+0.13	0.78	0.73
8	+0.07	+0.22	0.85	0.92
9	+0.22	-0.56	1.36	1.22

TABLE III

Charge densities  $q$  on the atoms of the individual planes of the low-index faces of Pt

Plane	Face		
	(100)	(110)	(111)
1	-0.16	-0.37	-0.14
2	+0.34	+0.75	+0.30
3	-0.16	-0.37	-0.14

suggests that the steps have increased reactivity, indicating their basic importance in the interaction of the chemisorbed gas molecules with the stepped (112) surface of the metal.

It holds for all the metals studied that the bond orders between the atoms of a single plane decrease in the direction towards the centre of the crystal.

#### *Nondissociative Chemisorption*

Nondissociative chemisorption was studied on the surfaces of the individual metals for ten different positions of capture of the N<sub>2</sub> molecule as shown in Fig. 4. The energy of nondissociative adsorption (energy gain) refers to scheme (A):



and is given in Table IV for the individual types of capture.

The total charge and the values of the bond weakening on the N<sub>2</sub> molecule adsorbed on the individual types of sites on the (112) crystal cross-section of the metals studied are given in Table IV. The highest values of the adsorption energies for capture of N<sub>2</sub> molecules above the individual atoms of V sites on the Ir and Pt surfaces correspond to energy preference for these types of capture of the N<sub>2</sub> molecules com-

TABLE IV

Adsorption energies  $E_{\text{ad}}$  (kJ mol<sup>-1</sup>) for nondissociative chemisorption, overall charge  $Q$  on the adsorbed N<sub>2</sub> molecule and weakening of the bond orders ( $-\Delta\rho$ ) in the adsorbed N<sub>2</sub> molecule for the systems studied

System	$E_{\text{ad}}$		$Q$		$-\Delta\rho$	
	Ir	Pt	Ir	Pt	Ir	Pt
IA	15	45	0.02	-2.96	0.05	1.88
IB	14	44	0.02	-2.96	0.05	1.88
IIA	22	28	0.01	-3.29	0.03	1.92
IIB	1	30	0.00	-3.06	0.04	1.89
IIIA	4	21	0.01	-3.18	0.02	1.92
IIIB	9	28	0.02	-3.02	0.03	1.89
IVA	0	14	0.01	-3.60	0.01	1.98
IVB	1	13	0.01	-3.58	0.01	1.98
VA	56	63	0.11	-2.75	0.12	1.85
VIB	0	13	0.01	-3.75	0.01	1.99



pared to the other systems studied. This fact is in agreement with the experimental result (for example see refs<sup>5,12,13</sup>). It has been found experimentally<sup>5</sup> that molecular nitrogen is adsorbed on the Pt surface in positions above the individual surface atoms<sup>5</sup> or in bridging positions<sup>13</sup>.

The capture of N<sub>2</sub> molecules above the individual atoms of the *V* sites on the Ir and Pt surfaces involves minimal electron flux to the N<sub>2</sub> molecules adsorbed on the Pt surface, or to maximal flux of electrons from the adsorbed N<sub>2</sub> molecule to the Ir surface.

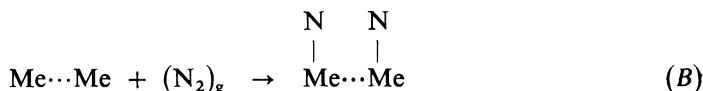
The presence of a charge localized on the atoms of the adsorbed N<sub>2</sub> molecule is connected with increasing weakening of the bond order in this molecule. It follows from the values listed in Table IV that this increase apparently depends on the absolute charge value localized on the adsorbed N<sub>2</sub> molecule.

The bond order of the adsorbed N<sub>2</sub> molecule is most weakened on its chemisorption on the Pt surface, where it also has the highest negative charge. The weakening of the bond order in the adsorbed N<sub>2</sub> molecule is virtually zero for the chemisorption of the N<sub>2</sub> molecule on the Ir surface. It follows from a comparison of these conclusions with the values of the overall charge localized on the studied surface of the pure metals (Table II) that the lower charge on the metal surface leads to a decrease in the charge value localized on the adsorbed N<sub>2</sub> molecule. As the absolute value of this charge increases, the weakening of the bond order also increases, i.e. the bond order is decreased in the adsorbed molecule.

These considerations suggest that on Pt surface the reactivity of adsorbed N<sub>2</sub> molecules for electrophilic reagents will be increased, whereas the Ir surface apparently has no appreciable effect on this reactivity.

#### *Dissociative Chemisorption*

Dissociative chemisorption was studied on the surfaces of the metals for the capture of N<sub>2</sub> molecules on multiple sites and for the dissociation of N<sub>2</sub> molecules in the sites above the individual atoms. The energy changes connected with dissociative chemisorption expressed schematically as



are listed for the individual types of capture in Table V. The studied types of capture for dissociative chemisorption are shown in Figs 5a and 5b.

Calculations of the chemisorption of molecular N<sub>2</sub> on the Pt and Ir surfaces studied indicated that none of the considered ways of dissociative sorption of N<sub>2</sub> on these surfaces is favourable. In fact on the Ir surface this process is definitely energetically unfavourable as compared to nondissociative adsorption. Thus, it can be expected

that chemisorption of molecular N<sub>2</sub> on the studied (112) crystal faces of the Pt surface will occur through the nondissociative mechanism in the positions above the individual atoms.

In all the studied systems, dissociative chemisorption involves electron flux from the metal to the chemisorbed N<sub>2</sub> molecule. In a theoretical paper<sup>10</sup> in which the results of the study of the chemisorption of N<sub>2</sub> on the Pt stepped plane are summarized it has been found that molecular adsorption predominates at low temperatures, and dissociative adsorption on "active sites" begins to occur at temperatures above ambient. However, the nondissociative adsorption continues to predominate because of the low contents of the "active sites" on the metal surface. Nitrogen molecules are similarly adsorbed linearly on iridium surface (refs<sup>14-17</sup>).

### CONCLUSIONS

The lone orbitals of the first three surface planes of the (112) metal surface studied react with molecules of chemisorbed N<sub>2</sub>. The effect on the mechanism of the chemisorption by the lone orbitals of the first two subsurface planes differentiates it from the mechanism of chemisorption on a smooth surface.

The energy values for chemisorption of N<sub>2</sub> indicate that the studied process occurs through the nondissociative mechanism on the (112) crystal faces of the Ir and Pt surfaces. This linear capture occurs primarily above the individual atoms of the metal surface.

It follows from comparison of the charge values on the chemisorbed N<sub>2</sub> molecule with the charge values localized on the studied surface of the pure metals that, the lower the charge value on the studied pure metal surface, the smaller will be the

TABLE V  
Adsorption energies  $E_{ad}$  (kJ mol<sup>-1</sup>) for dissociative chemisorption in the systems studied

System	$E_{ad}$		System	$E_{ad}$	
	Ir	Pt		Ir	Pt
<i>I-I</i>	-668	-206	<i>IVB-IVA</i>	-481	-31
<i>I-II</i>	-679	-213	<i>IVA-IVA</i>	-470	-18
<i>I-III</i>	-685	-217	<i>VA-VA</i>	-491	+3
<i>II-II</i>	-691	-221	<i>IVA-VA</i>	-480	-9
<i>III-III</i>	-702	-89	<i>VIB-VIB</i>	-531	-55
<i>II-III</i>	-697	-228	<i>IVB-VIB</i>	-510	-49
<i>IVB-VA</i>	-491	-23	<i>IVA-VIB</i>	-533	-110
<i>IVB-IVB</i>	-492	-50	<i>VA-VIB</i>	-511	-27

charge on the N<sub>2</sub> molecule adsorbed on this surface. Thus, it can be expected that the reactivity of the N<sub>2</sub> molecule chemisorbed on the studied (112) surfaces of Pt will be increased for electrophilic reagents, while chemisorption of N<sub>2</sub> molecules on the Ir surface apparently does not affect their reactivity.

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