COLORADO STATE
UNIVERSITY
FORT COLLINS, COLORADO
80521

department of electrical engineering

N71-34204

COLORADO STATE UNIVERSITY
Department of Electrical Engineering
Fort Collins, Colorado 80521

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A THIN POLYMER INSULATOR FOR JOSEPHSON TUNNELING APPLICATIONS

Semi-Annual Report

July 1971

C. W. Wilmsen

J. C. Robertson

NASA Grant No. NGR 06-002-094
Office of Research Grants and Contracts
Office of Space Science and Applications
National Aeronautics and Space Administration
Washington, D.C. 20546

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Introduction

In the previous reports we have outlined our basic studies of Josephson junction formation by the chemisorption of organic molecules and the design of specialized equipment to fabricate the monolayer and Josephson junctions. During the past six month period, we have experimented with Josephson junction formation with partial success. However, we have become increasingly aware that we must fully understand the chemisorption process before a complete monolayer can be successfully achieved. Therefore, we are presently placing the major emphasis of our research on the study of chemisorption and in particular, the chemisorption of organics on the Pb surface. Three methods are presently being used:

1. Carbon-14 labeled organics
2. Differential volume experiments on Pb powders
3. Computer simulation

In addition we are analyzing the effects of shorts and geometry on the electrical characteristics of Josephson junctions. Details of each of these are given in the following sections.

Those contributing to the research during this report period are:

Dr. Carl Wilmsen - Associate Professor, Electrical Engineering

Dr. Jerry Robertson - Assistant Professor, Electrical Engineering

Mr. Don Stuehm - Research Assistant, Electrical Engineering

Mr. Paul Hammer - Lab Assistant, Chemistry

Mr. Eric Osterholm - Lab Assistant, Chemistry

Mr. Dave Whittman - Research Assistant, Electrical Engineering

II. Josephson Junction Formation Experiments

Numerous attempts have been made to form a Josephson junction with an organic monolayer on Pb. Three different types of organics were used (Table I). Current-voltage measurements were made at room, liquid nitrogen and liquid helium temperatures. The results varied from no indication of a monolayer to partial coverage of the Pb with an organic.

The basic problems and approaches to monolayer formation were outlined in a paper presented at the March meeting of the American Physical Society. This paper is included as Appendix I. The following outlines the formation experiments and their results. All the organics are introduced into the vacuum as a double molecule which is attahced at their reactive ends (dimer). These are then broken up into two reactive modecules.

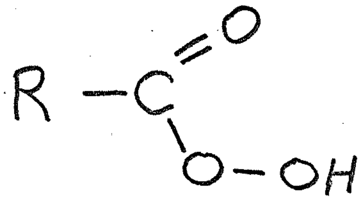
The first attempt at forming a Josephson junction since the last report was made using actoxy for the monolayer, the dimer was broken up by passing this Organic through a 250°C screen. The deposition was for 10^{-4} Torr seconds. Testing of the six junctions at room and liquid nitrogen temperatures indicated no barrier was present. An analysis of the organic indicated that the life time of the monomer was too short for it to reach and absorb onto the lead surface, unless the dimer is broken up at the Pb surface.

Organic II was the next used. It has a 14 carbon chain and should yield an insulator thickness of 16Å. The dimer was broken up using a 120°C substrate temperature. This organic was leaked in for 10^{-4} Torr seconds. Testing of the six junctions at room and liquid nitrogen temperatures indicated that no barrier was present.

The next set of junctions made with Organic II that was introduced for 1.2×10^{-3} Torr seconds on a 180 C substrate and tested at LHe temperatures.

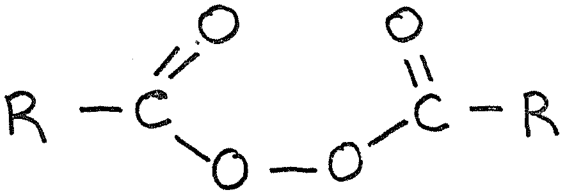
TABLE I

Organic I



Peroxymrystic Acid

Organic II



Acylperoxide

Organic III

$R-O-O-R$

Alkylperoxide

R is $CH_3-CH_2\cdots CH_2$

We wanted to make sure that the previous tests to determine if a barrier was present were valid. The room, liquid nitrogen and liquid helium temperature tests all indicated that no barrier was present. The liquid nitrogen tests were discontinued because they destroy some of the junctions.

The 180°C substrate of the previous experiment was close to the destruction point of the organic. The next set of junctions were built using a 25°C substrate and Organic II was broken up by passing it through a 100°C screen for 0.6×10^{-3} Torr seconds fed through a 25°C screen for $.6 \times 10^{-3}$ Torr seconds. The liquid helium tests showed that a weak link or excessive current device existed. The maximum current was insensitive to magnetic fields similar to a Josephson junction with shorts. The conclusion for this junction was that the organic did not cover the PB surfaces 100%.

We next attempted to increase the surface concentration of the organic. The substrate was heated to 100°C to break up Organic II closer to the lead surface but still not destroy the lead film and the organic. The organic exposure time was increased to 0.36 Torr seconds for increased surface concentration. The liquid helium tests indicated that only a short existed and no barrier was present. The heated substrate does not appear to be an acceptable method of breaking up the dimer.

Next Organic III was used because of its more desirable properties. The R-O-O-R was broken up by passing it through a 150°C screen for 1.8×10^{-3} Torr seconds. The liquid helium tests showed a weak link device indicating partial coverage.

In summary, the II and III organics partially covered the lead as indicated by testing the devices at LHe and observing a weak link or excess current characteristic. The organic deposition parameters (time, pressure, temperature) were varied to insure that (1) The dimer was breaking up into a monomer and (2) The organic concentration at the lead surface was sufficient for total coverage.

We conclude from those experiments that the organics used are absorbing onto the lead. Total coverage has not been achieved. Presently we are conducting tests with radioactive organics to determine what deposition parameters are needed for 100% coverage of the lead surface.

III. Chemisorption

As previously stated, it now appears that we must know much more about chemisorption of organics in order that the monolayer be successfully formed. We must determine the best method of breaking up the dimers, ways of obtaining a complete monolayer coverage of the Pb and the bonding energy of the organic on the Pb surface. To obtain this information we are using a radioactive carbon-14 method, a standard volumetric technique and computer simulations. There is some overlap of these techniques but each has a particular purpose in our research.

A. Carbon-14 Technique

This technique is relatively straight forward. The Pb is vacuum deposited and the organic introduced. One carbon of the organic is radioactive; giving off a 0.14 eV electron. After exposing the Pb in the desired manner, the system is opened and the Pb sample removed and placed in a counter. The background count is subtrated from the total count and compared with the count expected from a monolayer. The initial experiments show only a 10-25% coverage. This method is relatively simple and dependable and these experiments are continuing using more optimum conditions for absorption.

B. Volumetric Technique

With the volumetric technique, one starts with a known volume of the gas at the some pressure. The volume containing the absorbing sample is also known along with the surface area of the sample. The sample volume is evacuated to a pressure at least 1/10 that of the vessel containing the gas. The valve between the two volumes is then opened and the pressure recorded. If the gas does not absorb then the pressure will reduce to a value determined by the two volumes. However, if the gas does absorb then the pressure will be reduced further due to gases sticking to the surface.

This method requires skill and patience but it does yield information on dimer break up and rates of absorption. Our system is operating but no results have been obtained to date.

C. Computer Simulation

We continue to use a quantum mechanical computer simulation of chemisorption in order to study the absorption of organics. The results have appeared quite good but we have felt that since this technique had not been previously applied to chemisorption, we should test the method on a known system. We chose the carbon monoxide - nickel system. The computer results fit the experiment quite closely and will appear in the Journal of Vacuum Science and Technology. This paper is given in Appendix II.

IV. Analysis of Josephson Junctions

The Josephson equation , $J = J_1 \sin\theta$, describes the current density between two superconductors separated by a thin insulator. J_1 , which is related to the Josephson penetration depth (λ_J), has been assumed to be constant in previous analysis of the junction. A more realistic approach would be to assume that the barrier is uneven and hence J, would vary with position. The limiting cases would be (1) $J_1 = 0$ (an open in the barrier), and (2) a short across the barrier. These are of special interest to us, since the monolayers are not complete. This gives rise to shorts and opens. Therefore, we are presently solving the Josephson equation for the cases with the aid of a digital computer. The effects of magnetic fields are also investigated.

The case of an open in the barrier is of significance in analyzing and designing Quantum Interference Devices (two Josephson junctions in parallel). Our results are in excellent agreement with experiment and much better than previous theoretical work. A paper presenting this analysis is presently being prepared.

APPENDIX I

A Thin Polymer Insulator for Josephson Junction Applications

By

C. W. Wilmsen, D. L. Stuehm, J. C. Robertson

Presented to the American Physical Society

March 1971

A Thin Polymer Insulator for Josphson Junction Application

by

C. W. Wilmsen, D. L. Stuehm, and J. C. Robertson
Colorado State University
Fort Collins, Colorado 80521

At the present time Josephson junctions are formed by oxidation of the base metal. While this has produced useful junctions, one has little control of the insulator thickness which can only be assumed but not measured. In addition the oxygen can diffuse into the metal electrodes which is the principle cause of junction aging.

Today, I will present a different technique of forming the thin insulator. Basically, the technique consists of first depositing a superconducting metal in an UHV, introducing a vapor of large organic molecules into the vacuum, allowing the organic to chemisorb on the metal to form the insulator. A top metal is then deposited on the organic layer to complete the junction. Conventional vapor deposition would result in a thick layer which would be irregular and hard to control for the 10-20Å range required for tunneling. For this reason we use a carbon chain terminated on one end with a non-reactive CH_3 and the other end terminated by a reactive radical. The reactive end chemisorbs on the metal with a bond strength of the order of 10-100 kcal/mole while the non-reactive end only physically adsorbs with an energy of about 2-4 kcal/mole. The reaction of the second layer on the first is again a weak bond and therefore only a monolayer builds up. This is assured by maintaining the substrate at an elevated temperature which drives off the physically adsorbed molecules.

The advantages of such an insulator are obvious.

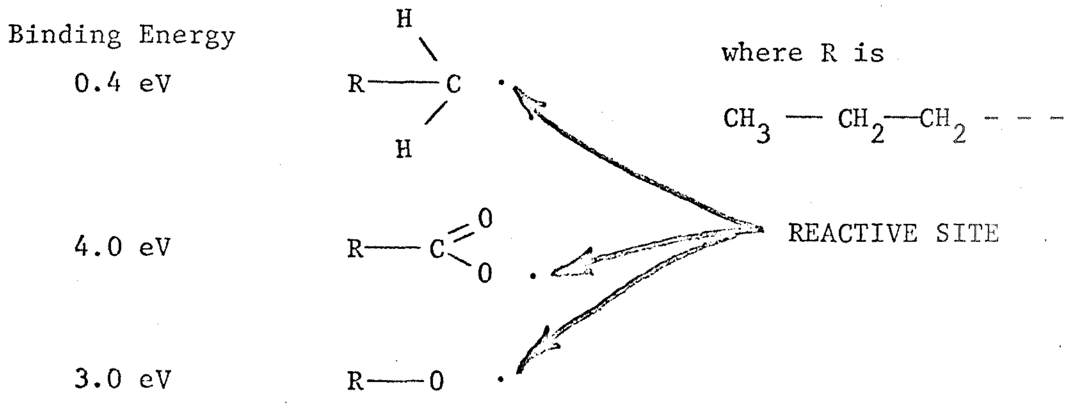
a) The large molecules do not diffuse into the metal layer hence preventing aging.

b) The thickness of the insulator is known, the length of the molecule standing on the metal.

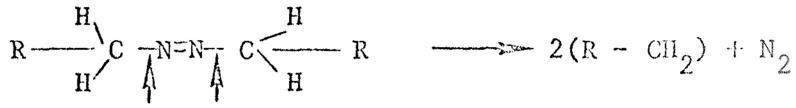
c) The thickness can be easily varied by changing the chain length - one can then experimentally study the coupling energy of the junction.

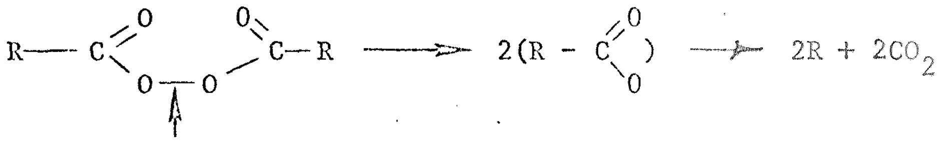
This technique of forming the monolayer from a vapor is similar to the Langmuir-Blodgett (1-3) method of dipping the substrate through a monolayer floated on water. The important difference, however, is that the metal film is not exposed to the atmosphere or the water bath.

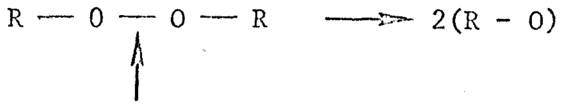
In order for the vapor technique to work properly, the reactive end of the organic molecules must form a strong chemical bond with the base metal. We have chosen to work with Pb which is relatively inert to most organics. We have carried out Extended Huckel Molecular Orbital calculations (4) and found that in order to chemisorb, the organic adsorbate must be oxidative. The three most promising radicals are:



These partially oxidize the Pb surface. Since these are reactive they are introduced into the vacuum as dimers:

1.


2.


3.


To form the monomer molecules, the bonds indicated by arrows must be broken. This can be accomplished by heat; either at the substrate or in the vapor stream approaching the substrate. In the case of dimer 2 the monomer decomposes to R + CO_2 in about 10^{-9} seconds. Therefore, the dimer must be broken down at the hot substrate surface, since the transit time from a hot filament 1 cm away would be $\sim 10^{-4}$ seconds. This decomposition to R + CO_2 creates a competition between the adsorption of the monomer, R + CO_2. The CO_2 will only physically adsorb and therefore does not interfere with the monolayer formation. The hydro-carbon chain, R, will chemisorb, in fact, it is the same as monomer 1, but not as strongly as the acyl monomer. This will cause an irregular surface with a variation in thickness of 2-3Å. Dimers 1 and 3 are more stable and can be broken down either at the substrate or at a filament. Another consideration is the vapor pressure of the dimer and the duration of substrate exposure to the vapor.

The vapor pressure of the dimer has been found to decrease rapidly as R is increased. However, adequate vapor pressure is available for R up to 16. with R=18 the vapor pressure is low even with heating up to 100°C.

The exposure must be greater than 10^{-6} Torr sec. in order to obtain a monolayer coverage. For a hot substrate the sticking coefficinet for the dimer, which first physically adsorbs, will be low, of the order .001 to .01. Therefore, the exposure must be 10^{-3} to 10^{-4} Torr sec.

Introducing the organic vapor at a pressure of 10^{-6} Torr, this requires exposure times of 100 to 1000 sec. or about 2 to 20 minutes.

We have begun to experiment with these techniques to form the monolayer. The major problem is obtaining experimental information on the adsorption. It appears best to conduct these experiments in a special apparatus.

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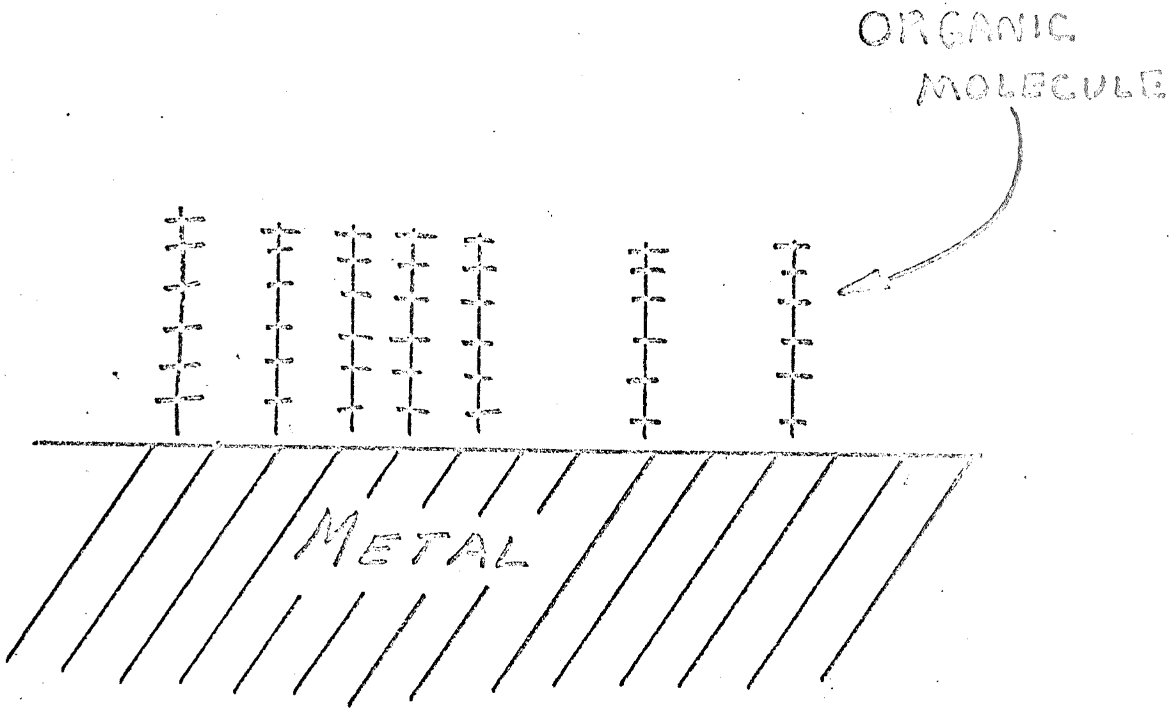
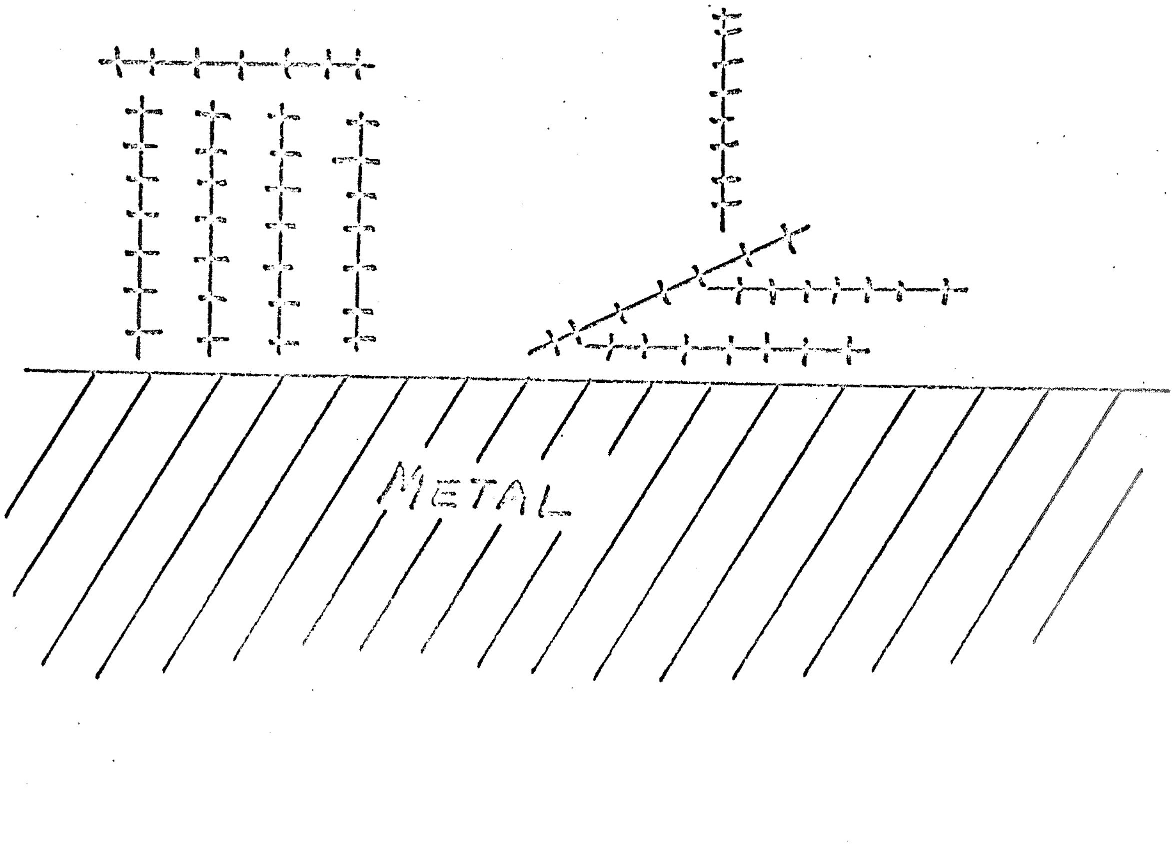
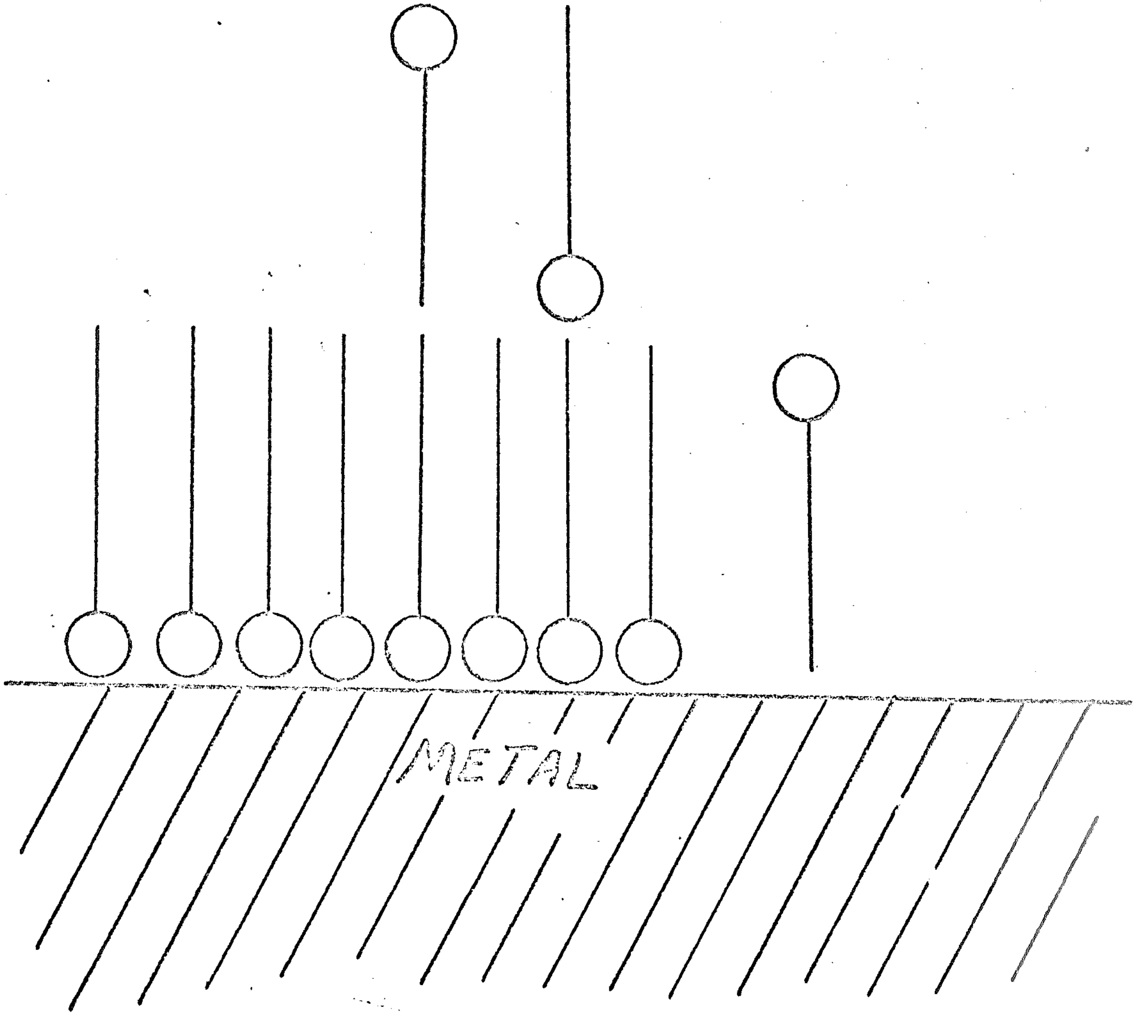

ORGANIC
MOLECULE
METAL


METAL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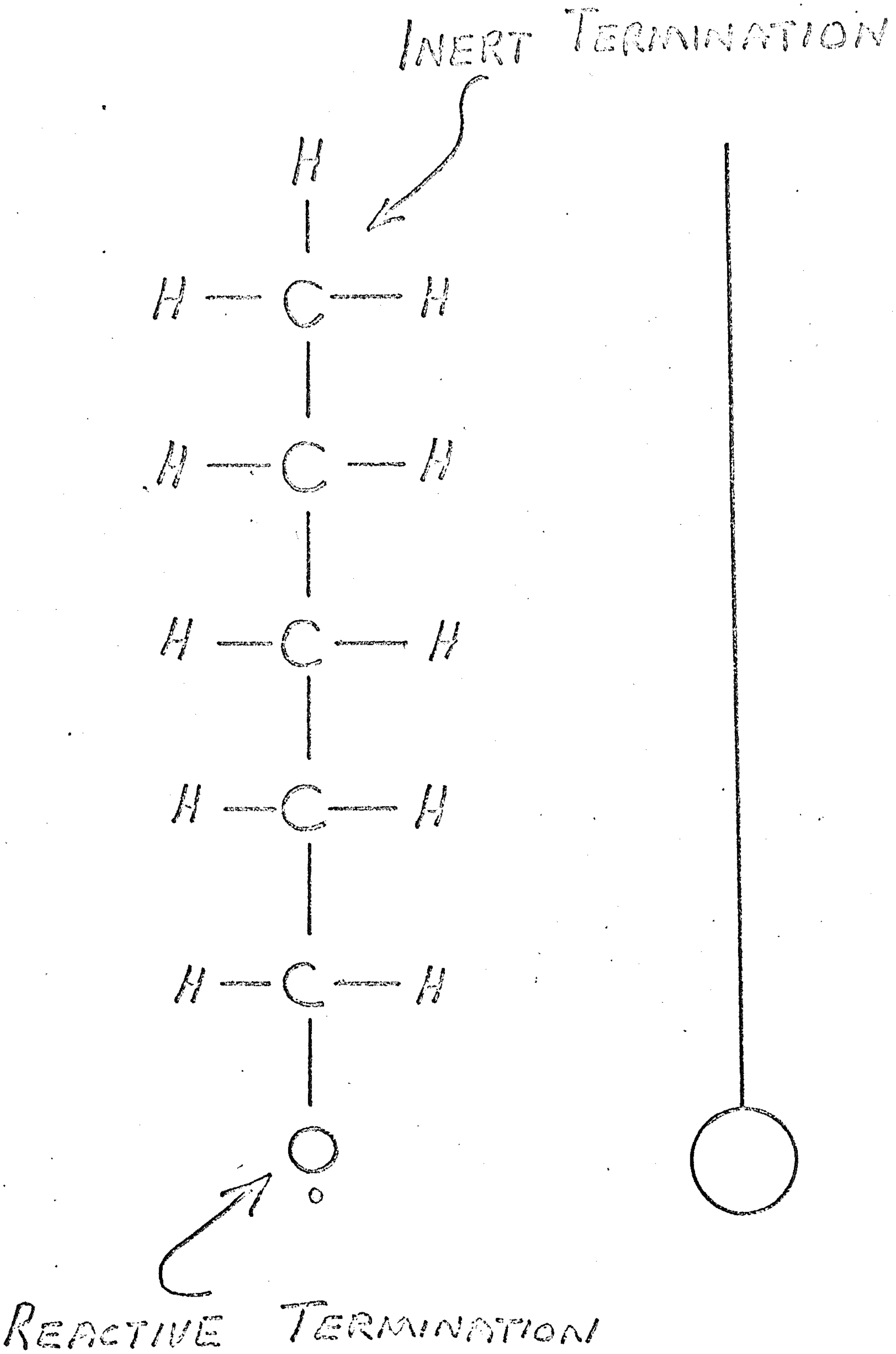

MOLECULE SYMBOL

$CH_3-(CH_2)_4-O\cdot$

APPENDIX II

Preferential Orientation of CO Absorption on Ni as Determined by Extended Huckel Calculations

By

J. C. Robertson and C. W. Wilmsen

Journal of Vacuum Science and Technology

Preferential Orientation of CO Adsorption on Ni as Determined by Extended Huckel Calculations*

J. C. Robertson and C. W. Wilmsen
Colorado State University
Fort Collins, Colorado 80521

ABSTRACT

The adsorption of CO on the nickel surface has been calculated using a modified extended Huckel technique for a number of different orientations of the CO with respect to the nickel surface. The calculations show that double site adsorption with the CO molecule normal to the surface and the carbon atom closest to the metal gives the most stable configuration (2.57eV). The single site absorbs with an energy of 2.39 eV. However, other configurations also give fairly large bonding energies. The CO normal to the surface with oxygen closest to the metal given a heat of adsorption of 0.37 eV. Two center adsorption with the CO axis parallel to the surface and the molecule symmetrically placed between the nearest neighbors gives a chemisorption energy of 1.34 eV. These values compare with an experimental value of 1.98 eV. It is interesting to note that when the CO bond is stretched 10% in the latter configuration the total energy of the system decreases rather than increases.

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*This work supported in part by NASA Headquarters, Washington, D. C.

I. INTRODUCTION

The extended Huckel molecular orbital (EHMO) theory has recently been applied to the study of chemisorption.[1-3] The technique has great potential for calculation of chemisorption energies, surface mobility, and local interaction on the surface. However, criticisms have been applied to the EHMO technique. The most serious of which is the failure to take into account spin orbitals and the two, three and four centered electron repulsions. These same criticisms were applied to the simple Huckel technique for π-systems and yet the Huckel π-electron calculations have been found surprisingly useful to the practicing organic chemist. For their chemisorption calculation of C, O and N or graphite Bennett, McCarroll and Meissner[2] report that the EHMO method gave physically unreasonable charge transfers between the adsorbate and the surface while for H the EHMO technique gave encouraging results.[3] Previously we reported useful results for organic molecules adsorbing on a Pb surface.[1] Therefore, while the EHMO technique has been successfully used form some chemisorption calculations, there still remains doubt about its applicability. The purpose of the present work is to apply the EHMO technique to an adsorbate-adsorbent system for which there is well documented experimental data. For this reason we have chosen to investigate the CO on Ni system.

Calculations were made to obtain qualitative information on the preferred orientation of the CO molecule on the Ni surface and semi-quantitative information on the relative binding energies and surface barriers to movement. In addition, we have calculated the relative energy for the disproportionation reaction by the Rideal type mechanism.[4]

II. METHOD OF CALCULATION

We have used a semi-empirical one-electron molecular orbital technique for chemisorption calculations. The program was originally written by R. Hoffman[5a] and we are using the version modified by L. C. Cusachs.[5b] The calculations are carried out on a CDC 6400 computer. The input parameters for the program are the valence state ionization potentials and the orbital parameters for the Slater type orbitals.

The <100> surface of nickel has been chosen since this surface has been extensively studied. The size of the surface is somewhat arbitrary being limited by the desire for a reasonable surface on the one hand and expensive computer time on the other. Within these limitations we have chosen an eight nickel surface. This allows us to have two central nickel atoms for adsorption sites away from edge effects. For the surface coverage studies the edge atoms were used without apparent problems. The size of the surface plays a very limited role on the relative energy of chemisorption. In Figure 1 we show a 15 nickel atom surface with an adsorbed CO in the center. The numbers indicate the magnitude of the Lowden charge on each nickel atom. This is compared with the similar situation on the eight atom surface we used in our calculations. The rapid decrease of the charge with distance from the adsorbent site indicates the local nature of adsorption and justifies using a small surface.

In as much as this molecular orbital technique is not useful for determining bond lengths we have chosen to use a consistent value of 1.75Å the Ni-C length and a value of 1.128Å for the C-O bond length. This distance for the Ni-C bond is close to the distance for maximum overlap population for this bond (maximum population at 1.5Å) and is a compromise between the bond distance of nickel carbonyl (1.82Å) and the position of maximum overlap.

III. SURFACE ORIENTATION OF ADSORBED CO

If a theoretical approach is to have any value it must first of all be able to predict such gross effects as the correct orientation of the CO molecule relative to the nickel surface. An octet diagrmm for CO shows that each atom is sharing six electrons in a covalent triple bond plus a coordinate covalent bond directed from oxygen to carbon. In addition each of the two atoms has an unbonded electron pair capable of bonding to a Lewis acid such as the metal surface. One would postulate therefore that either atom could bond to the surface, although experimentally it is found that the carbon bonds to the Ni surface. Table II summarizes the EHMO energy calculations comparing them with other theoretical calculations and experimental results. The EHMO calculation yields a much tighter binding for the CO molecule normal to the surface (configurations I and II) with the carbon nearest the surface compared with the oxygen nearest the surface (III) or the molecule in the plane of the surface (IV). This is in accord with experimental observations.

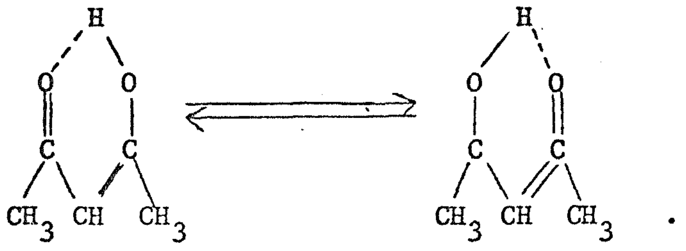
IV. PREFERRED SITE LOCATION AND SURFACE MOBILITY

Previous reports on the preferred site location of CO on Ni are not fully in agreement. However, most definitely it is configuration I or II or possibly a combination of the two. Degras[9] found that the bridge site (II) was dominate; covering approximately 6 x 10^{14} cm^{-2} sites of the <110> surface with a bonding energy of 1.98 eV. Park and Farnsworth[10] found that the <100> surface favored bridge bonding (II) and the <110> surface favored single bonding (I). Den Besten[11] et al. report that both the bridged and the single sites absorbed with a strong bond. Their magnetization-volume isotherm results are in agreement with the infrared studies of Yates and Garland.[12] Klier et al.[13] found little difference between CO adsorption energy on the <100> and <110> Ni surfaces. Both surfaces bond with about 1.1 eV.

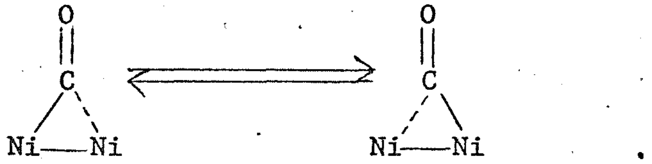
Eischens and his co-workers[14,15] report that both single and bridged site absorption occurs with relative amounts of each dependent on the nature of the support and the surface coverage. Brennan and Hayes[16] also report that both single and bridge sites adsorb with an energy of about 1.8 eV.

Using the EHMO technique we calculate a binding energy of 2.53 eV for the bridged CO and 2.37 eV for the single bond. This indicates that while the bridge site is preferred (by 0.17 eV) the small difference in energy between the two sites would make the two sites competetive and hence both should be observed. The magnitude of the EHMO calculated bonds compares reasonably well with the experimental values of 1.98, 1.8 and 1.1 eV reported by various researchers. Grimley,[17] using Hartree-Fock perturbation methods, calculated 2.2 eV for the single bond.

A closer examination of the bonding energies reveals that the preferred site is not symmetrically located between two Ni atoms, but is rather somewhat off of the center. The bonding to the two Ni atoms is not the same; being stronger to the closest atom. The CO bonding energy curve (Figure 2) shows that two shallow energy wells exist. It is likely that the CO molecule is located at the site corresponding to one or the other of the two potential wells and is in rapid thermal fluctuation due to the low barrier between them. This fluctuation (tautomization) is known to occur in other systems such as the enol form of 2,4 pentandione shown below.



The CO tautomization would be



There is a barrier of 0.05 eV to this fluctuation.

Surface mobility should also be high since a barrier of only 0.2 eV separates briging sites. This is in accord with experimental observations.[13]

V. SURFACE COVERAGE

The surface coverage of the <100> face of Ni was investigated by placing two or three bridge bonded CO molecules on an eight atom surface as shown in Figure 3. The CO placements simulate a random or criss-cross distribution of non-touching CO molecules (a), rows of non-touching molecules (b), and two types of alternating rows of touching molecules, (c) and (d). Arrangement (a) was found to be energetically most favorable by - 3.50 eV, followed by arrangement (b) - 2.28 eV and arrangement (c) - 0.95 eV For convenience, arrangement (d) is used as a reference, i.e., zero energy. The total system energy of arrangement (b) has been adjusted by the energy of one free CO molecule in order to compare this two molecule arrangement with the three molecule arrangement.

In addition, the average CO molecule binding energy of arrangement (a) is 2.68 eV/CO molecule which compares quite well with the single molecule bridge bond strength of 2.57 eV. The other arrangements have much lower average binding energies: (b) - 2.06 eV, (c) - 1.23 eV and (d) - 0.92 eV.

For the bridge bonded molecules, the above data indicates that a random distribution of non-touching molecules is the most probable arrangement. This gives a saturated coverage of one CO molecule for each two Ni surface atoms, which is in agreement with experiment.[9]

VI. DISPROPORTIONATION

Various authors,[11,18] have reported that on desorption from a nickel surface at elevated temperatures, some carbon monoxide disproportionates to CO_2 and C. This process apparently competes with disorption to the extent that the atmosphere above a hot nickel surface may have 25% of the carbon present as CO_2. Several mechanisms may be easily envisioned for this reaction ranging from an attack by gaseous CO on adsorbed CO following a Bonhoeffer and Farkas type mechanism to a Rideal mechanism where a CO dissociates into adatoms and the oxygen is picked up by an adjacent adsorbed CO. We have made calculations for the first step of the latter reaction; the dissociation of CO on the surface into adatoms.

The results are shown in Figure 4 which gives the energy for a bridge CO molecule in the vertical position, the CO molecule tilted to the side, and the horizontal CO with normal to twice the normal bond length. It is seen that there is a barrier of 1.23 eV to changing the CO orientation from vertical to horizontal but once horizontal, the separation of C and O is exothermic.

VII. SUMMARY

The extended Huckel energy calculations presented here correctly predicted the preferred orientation and site location of CO on Ni. The binding energy magnitudes were also in good agreement with the experimentally observed values. The confirmation given by these calculations are convincing evidence for the validity of the EHMO technique applied to chemisorption. Our more detailed calculations provide insight into the nature of the adsorption sites and surface coverage that cannot be obtained experimentally.

TABLE I. Valence-state ionization potentials and orbital parameters for the EHMO calculations.

Atom	Orbital	n	z	H_{ii}(eV)
carbon	2s	2	1.50	-17.54
	2p	1	1.06	- 8.98
oxygen	2s	2	2.04	-29.10
	2p	1	1.35	-14.14
nickel	4s	2	0.95	- 7.93
	3d	1	1.68	-15.17

TABLE II

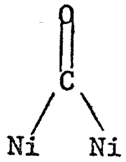
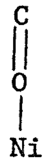
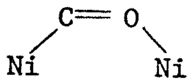
	Configuration	EHMO	Other Theoretical	Experimental
I.		2.39 eV Preferred Orientation		.17 eV [9] Preferred Orientation
II.		2.52 eV Preferred Orientation and Site	2.20 eV	1.98 eV [9] 1.8 eV [16] 1.1 eV [13] Preferred Orientation and Site
III.		0.37		
IV.		1.34 eV		

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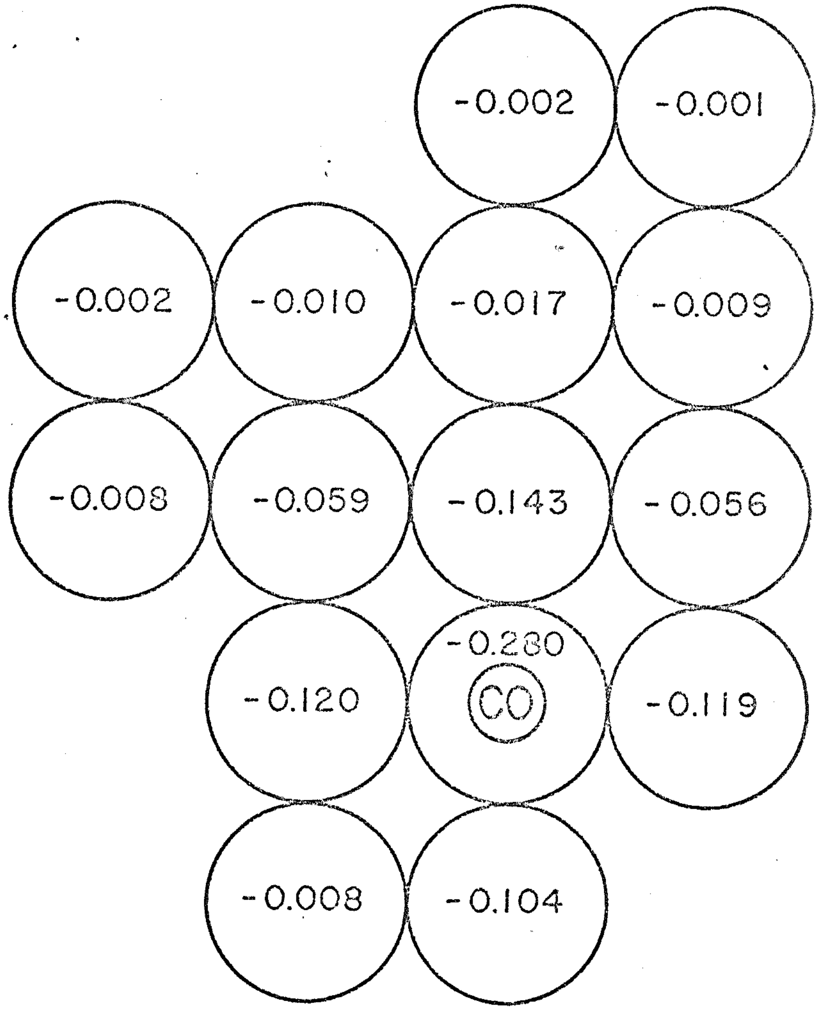
FIGURE CAPTIONS

Figure 1. The Lowden charge distribution on a 15 atom <100>surface of Ni with one CO molecule located 1.75 Å above the surface.

Figure 2. Energy contour for a vertically oriented CO molecule with the carbon atom 1.75 Å above the surface.

Figure 3. Four arrangements of bridge bonded CO molecules on an 8 Ni atom surface. The energies are relative to arrangement (d).

Figure 4. Possible disproportionation path. Vertical bridge bond → tilted → horizontal → horizontal with stretched bond.


-0.002
-0.001
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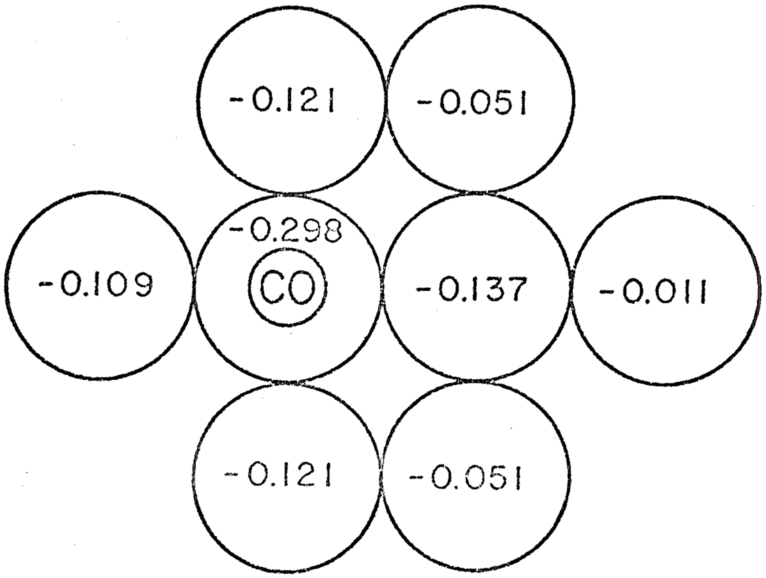
-0.056
-0.120
-0.280
CO
-0.119
-0.008
-0.104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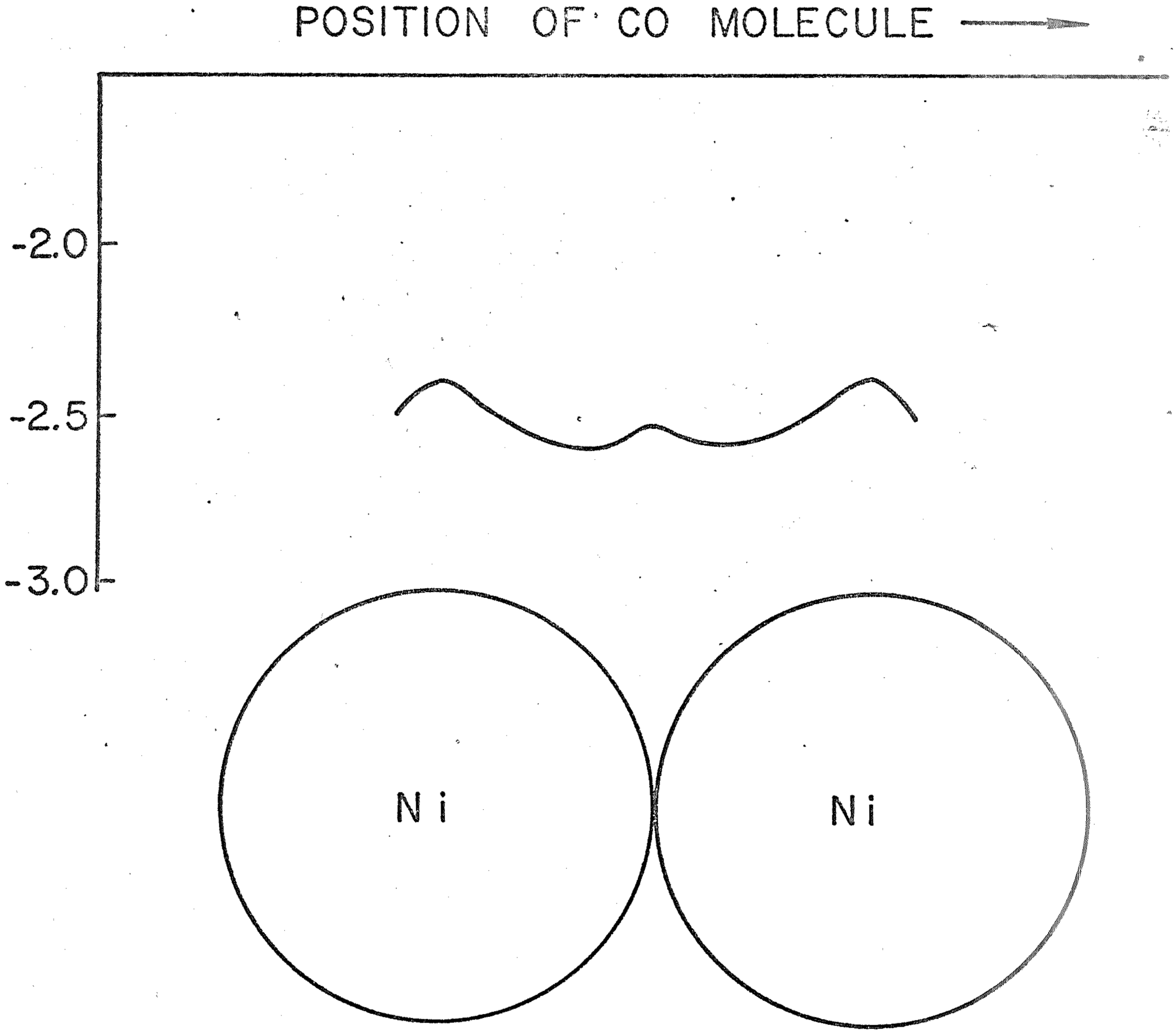
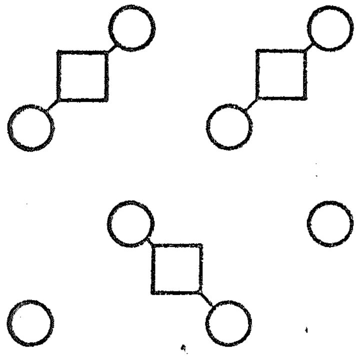
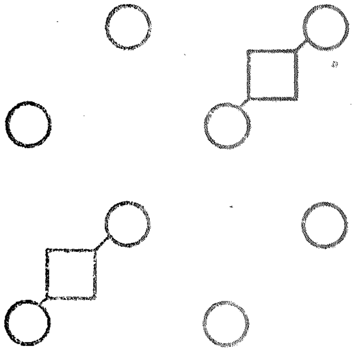
-0.051
-0.109
-0.298
CO
-0.137
-0.011
-0.121
-0.051


POSITION OF CO MOLECULE
-2.0
-2.5
-3.0
Ni
Ni



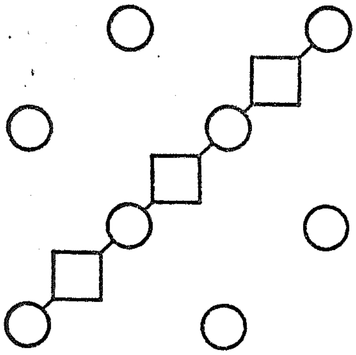
-3.50 eV

(a)



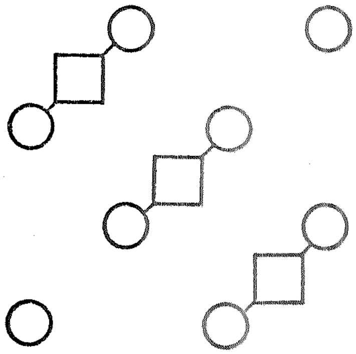
-2.28 eV

(b)



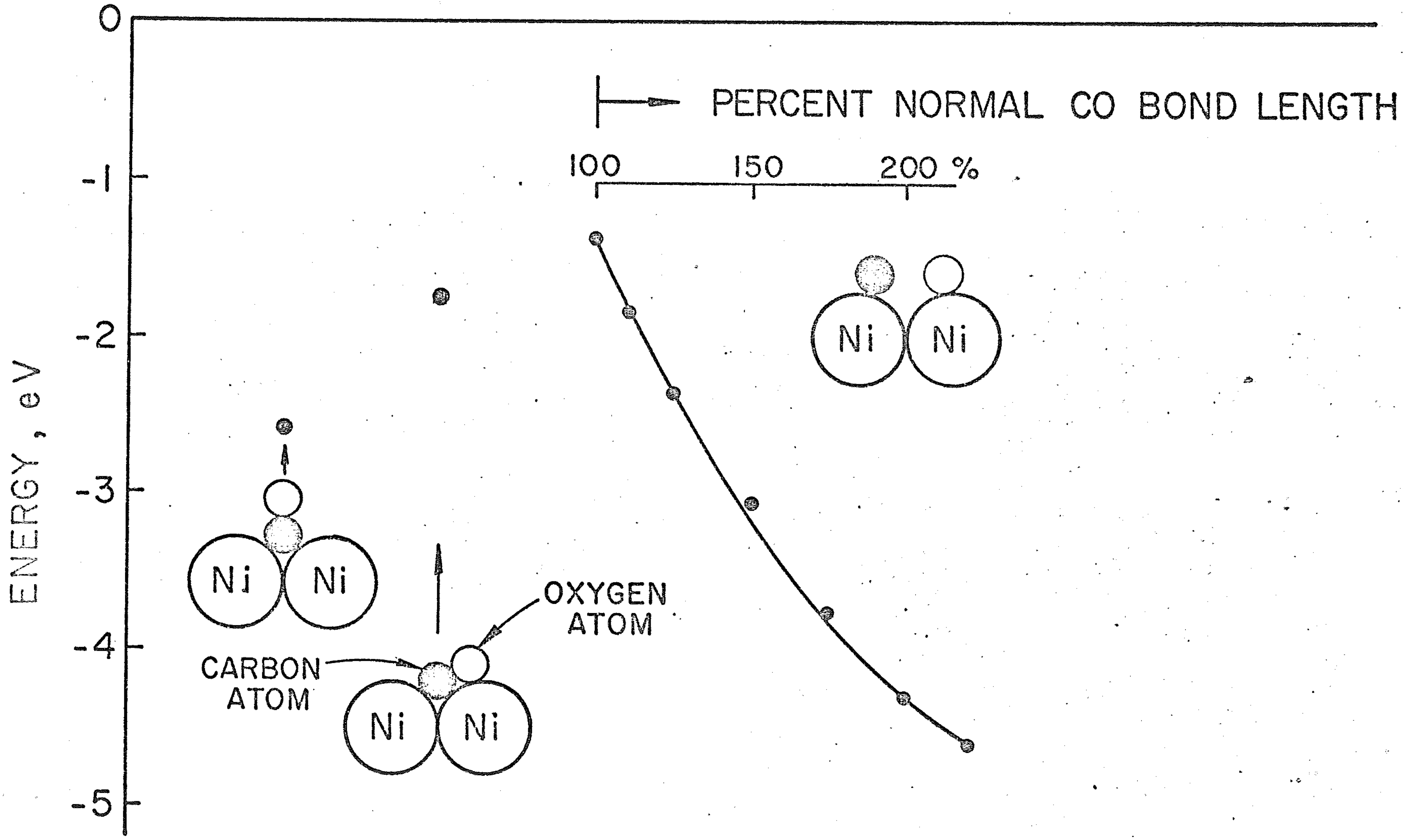
-0.95 eV

(c)



0.00 eV

(d)


0
-1
-2
-3
-4
-5
ENERGY, eV
PERCENT NORMAL CO BOND LENGTH
100
150
200 %
Ni
Ni
OXYGEN ATOM
CARBON ATOM
Ni
Ni
Ni
Ni