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CHEMISORPTION AND REACTIONS OF CLUSTERS OF NICKEL ATOMS*

by

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ABSTRACT

Recent work (1)(2)(3) with collaborators Frank Averill, Don Ellis, and Ron Yu (3) indicated that several things occur as an atom or a molecule approaches a surface. First, substantial shifts occur in the electronic levels of the molecule and are dependent on the height and orientation of the molecule above the surface cluster. Second, related shifts also occur when the basis set includes orbitals from the nickel atom plus the orbitals of the molecules. Third, as indicated by our population analysis, charge transfer from the metal occurs in the several cases studied to date. (1)(3) Fourth, when charge transfer occurs, all of the energy levels of the cluster are shifted but the individual shifts are not uniform. (1)(3)

In order to make reasonable comparisons with experimental results such as from photo-emission spectra and ESCA data, the effect of removing a fraction of an electron from various parts of the cluster has been investigated (3) since such a change in the electron population influences all of the energy levels of the cluster.

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This is the so-called relaxation effect. In Slater's theory of the transition state,⁽⁴⁾ the removal of only half an electron does give yield ionization potentials for atoms. Several prescriptions have been used which differ in the atomic portions of the cluster from which the electron is removed.

In order to provide additional insight into the behavior of small metal particles, several clusters of different symmetry containing five to nine nickel atoms have been studied. To put it briefly, it was found that the energy range of primarily d-like states is not significantly different from the width of the d-band in nickel metal, as long as the interatomic distance was comparable to that in the bulk metal.

INTRODUCTION

It is appropriate to discuss two separate issues in this lecture [as well as the interaction between them]. The first is the nucleation and growth of metallic clusters on a substantially amorphous substrate; this will be confined to geometrical and electronic structure of the clusters. The second is the approach of one or more molecules to the cluster; this will be exemplified by either the hydrogenation of acetylene, or the reverse reaction, namely the dehydrogenation of ethylene. The one-electron energy levels in both the approaching species and the cluster are affected by the distance separating the cluster and molecule. They are also affected by the relative orientation of the molecule even when the overall symmetry is unaffected. This arises from the fact that for

the total cluster (consisting of the metallic atoms plus those in the molecule) possessing a symmetry such as C_{2v} , very few degeneracies are required.

An analysis of carbon dioxide approaching a nickel cluster was reported recently.⁽¹⁾⁽²⁾ Strong evidence was obtained that electron transfer did occur from the nickel when a level, which was empty in the free molecule, was brought down into the vicinity of the Fermi level by the proximity of the molecule and metallic cluster. This process has been studied in greater detail for the adsorption of oxygen and sulphur on a (100) nickel surface and the conclusion concerning electron transfer supported by those self-consistent charge calculations.⁽²⁾⁽³⁾ Space does not permit us to discuss the method of making these calculations. The interested reader is referred to several recent papers.⁽²⁾⁽³⁾⁽⁵⁾ The results are in reasonable agreement with experimental data, although some caution must be exercised since the physical changes necessary to bring about the photon-emission in UPS and a fortiori in INS have not been incorporated into this model, or in any model of which the authors are aware. These results lend credibility to the conclusions drawn from the information on ethylene and acetylene which will be presented below even though the latter are not self-consistent since the conclusions "predicted" from similar non-self-consistent results with O, S and CO were borne out. These should be regarded as plausible results assembled for this lecture before the full story is known.

METAL CLUSTERS

The long-standing problems of nucleation and growth have been studied extensively but principally in terms of thermodynamics and reaction kinetics of the phenomena. There are several excellent reviews of this topic.⁽⁶⁾ A central precept of the conventional treatment of heterogeneous nucleation is that one can use the cohesive energy per atom (E_c/atom) obtained for the bulk metal to calculate the "chemical" or volume contribution to the free energy of an N atom cluster and can treat the surface energy⁽⁷⁾ as a quantity to be obtained principally from an analysis of extensive experimental work on kinetics of nucleation and growth. The experimental value of the surface energy, E_s , so obtained from data on homogeneous nucleation, has been shown by Turnbull⁽⁸⁾ to be $0.45 E_c$ for most metals and as low as approximately $0.32 E_c$ for complex systems. This result is striking. In the bond-breaking models, a surface atom has only lost four of its 12 nearest neighbors (on a high symmetry plane of a FCC structure: a comparable figure applies to BCC structures). By losing only about 25 per cent. of its nearest neighbors, an atom loses more than 55 per cent. of its binding or cohesive energy. This suggested to the authors that the equilibrium spacing in small clusters should be investigated. What follows is a partial account of this lead.

There are four or five approaches to interatomic potentials with which to evaluate the geometrical structure of a cluster. The first is the Morse potential. Its two coefficients are chosen to

give good fit with experimental data on interfaces⁽⁹⁾. The second is the general algebraic approach (in general, a sixth degree polynomial)⁽¹⁰⁾ such as Johnson and Wilson used. Here the increased number of coefficients permits one to obtain a much better fit by using various kinds of experimental data such as phonon spectra, neutron diffraction, compressibility, etc. A third version is the quantum mechanical approach adopted by Ho⁽¹¹⁾ and by Rao⁽¹²⁾ who used the pseudopotential method which was subsequently modified by a dynamic dielectric response of the medium. Although this approach is straightforward, in practice many approximations and correction factors had to be applied to obtain good agreement with data. Most of the tactics are reviewed in an earlier Battelle Colloquium on Interatomic Potentials and Simulation of Lattice Defects. As a general statement, the atomic positions and the relative energy of a variety of lattice defects are found fairly well for three or four metals but fail to lead to good results for others, such as transition metals. Thus, great reliability cannot be claimed for the predictive power when one or two pieces of experimental data may not be available, i.e. the coefficients do not lend themselves to an independent evaluation.

Ideally the fourth approach, i.e. the use of the Hellman-Feynman theorem,⁽¹³⁾ should be the best quantum mechanical method for calculating the interatomic forces since it takes all of the interactions, inter-electronic, electronic-ionic and inter-ionic, into account. Slater⁽¹⁴⁾ has shown that the multiple scattering-scaled

exchange method (MSX) of making molecular calculation developed by K. Johnson and Slater together with their collaborators⁽¹⁵⁾ can be vigorously applied if a single value of α is used as the scaling parameter throughout the region of interest. Application of the Hellman-Feynman theory to molecules has not led to good results as Deb⁽¹⁶⁾ noted in a recent review. At this stage, the difficulty appears to be in the quality of the wave functions available for molecules which involve even a small number of electrons. While the use of MSX orbitals in evaluating the Hellman-Feynman theorem is being actively pursued in several laboratories,⁽¹⁷⁾ it is premature to decide that it is sufficiently reliable for the present purposes.

A fifth method has been suggested by Waber.⁽¹⁸⁾ It is a modification of the method developed by Fröhlich⁽¹⁹⁾ for calculating the cohesive energy of alkali metals and extended by Raimes⁽²⁰⁾⁽²¹⁾ to polyvalent metals. Waber⁽¹⁸⁾ recently reported an evaluation of the Fröhlich-Raimes method for a relatively large number of metals subject to the limitation that there is only one adjustable parameter and this was to be independently found from the n^{th} ionization potential where n is integral number of free or conduction electrons assumed for each metal. Bolsaitis et al.⁽²²⁾⁽²³⁾ have used a much more parameterized version of this basic theory which they have labelled the Electron Cell Theory. They have obtained very good agreement with thermodynamic data of solid solutions of the noble metals Cu, Ag and Au as well as for these three unalloyed metals.

It was noted in the article by Johnson and Wilson⁽²⁴⁾ that gold was a particularly interesting test case since the previous interatomic potentials could not discriminate between the stability of various types of lattice defects in gold on the basis of their energy. The agreement of the shock-wave data on gold with that calculated by means of the Fröhlich-Raines (FR) model was not particularly good as noted some years ago in a preliminary report by Larson and Waber.⁽²⁵⁾ However, substantially improved agreement could be obtained by including a Born-Mayers type of repulsive term, namely $b \exp(-s_{ij}/r_{ij})$, to take account of the interaction between neighboring ion-cores;⁽²⁵⁾ the original FR theory assumed that they are negligibly small.

Recently Yu and Waber⁽²⁶⁾ have investigated the stability of two dimensional arrays of aluminum and gold. The (100) arrangement of 49 atoms one atom thick was very sensitive to the potential used and in some cases involving the potential for Al was dynamically unstable, whereas the hexagonal arrangement characteristic of the (111) plane was stable. Similar studies have been carried out for gold as well as studies of a variety of lattice defects such as crowdions and split interstitials; these results will be reported elsewhere.⁽²⁶⁾

The computer program used in this work is similar to those discussed by Beeler et al.⁽²⁷⁾ in the Battelle Colloquium and identified as GLOB. The lattice spacing of 49 gold atoms on a (100) plane shrinks significantly if the unmodified FR potential is used but expands if the coefficient ρ in the denominator of the exponential

term is too small. The more elaborate Bolsaitis energy expression leads to almost no change in the interatomic distances in gold. By a judicious choice of the coefficient ρ , namely 0.28 Bohr units, in the YW expression, we can obtain very good agreement with the interatomic force law calculated from the Bolsaitis expression. Better agreement could undoubtedly be obtained by further adjustment of the two parameters r_0 and ρ , or Slater exchange coefficient σ_s .

A similar study⁽²⁶⁾ has been carried out on nickel. We can obtain good agreement with shock-wave equation of state, i.e. compressibilities, by assuming that the effective number of electrons n is three and that nickel is too compressible if the valence is assumed to be two. If the FR energy expression is based on $n = 3$, a (100) sheet of 49 nickel atoms collapses. It is interesting that both a two dimensional hexagonal array [characteristic of the (111) plane] and a FCC unit cell are dynamically stable, though their equilibrium interplanar spacings are smaller than the bulk lattice parameter. Such difficulties can be avoided by adding the exponential term as Yu and Waber did for gold. A stable (100) array of 49 atoms shows only slight corner bulging of 1 or 2 per cent. if we use $n = 2$ and $\rho = 0.28$ Bohr. The results on small clusters which might be heterogeneously nucleated will be discussed in the lecture but there is not sufficient space to go into details here. The purpose of this discussion in which we have invoked an approximate energy expression to obtain an interatomic force law is to be a caveat, that the interatomic spacings and

conformation of small metal clusters consisting of only a few atoms may not be identical with those in the bulk metal. Characteristically Johnson and colleagues⁽²⁸⁾ have used standard interatomic distances and derived a considerable amount of useful information about energy levels therefrom. While there is merit in finding out how few atoms, separated by the normal equilibrium distance, would lead to a good representation (assessed by the energy range of a d-band in a transition metal) of the bulk metal, it is not clear that answering this question is relevant to small clusters on a supported catalyst. Although Johnson⁽²⁹⁾ has reported that a free icosahedron of atoms is more stable than a simple cube, the authors are unaware of any detailed attempts to settle this broad question of spacing and shape of smaller clusters.

LEVEL SHIFTS IN ACETYLENE AND ETHYLENE

The variety of reactions of olefins on catalytic surfaces is of great industrial and technological importance. It is well known that the dehydrogenation of ethylene to form acetylene occurs readily on a nickel surface at moderate temperatures.⁽³⁰⁾ Also the hydrogenation of acetylene can proceed on the same catalyst if the pressure is high and the equilibrium is shifted in that direction. The direction from which the hydrogen approaches is an interesting question not readily answered by experiment. However, quantum-mechanical calculations offer some hope of answering this question.

It is argued⁽³²⁾ that the hydrogens are adsorbed into the metal. A cluster of nine nickel atoms has been used to represent the first two layers of a (100) surface of a FCC metal. For our present purposes, we have used the interatomic spacings characteristic of the bulk metal. We have used the same nickel cluster so as to maintain some continuity with the results on oxygen and sulfur⁽³⁾ and carbon monoxide.⁽²⁾ Both acetylene and ethylene can be oriented over the cluster to maintain the C_{2v} symmetry. For example, the four hydrogens of C_2H_4 can either be in a vertical plane containing the perpendicular to the (001) plane as in Fig. 1 or lie in a horizontal plane containing the two carbon atoms. In treating the approach of hydrogen atoms to the acetylene, they can either lie in a plane containing the (100) direction as well as the two carbons (arrangement A of Fig. 2) or lie in the plane which is perpendicular to the internuclear C-C line and bisects this bond (arrangement B). These arrangements would be compatible with the hydrogen atoms coming from the interior of the metal (where it had been absorbed) and passing between two equidistant Ni atoms in the (001) surface, as shown in arrangement B. The symmetry is not altered if both of the hydrogen atoms of the pair are either of the heights indicated by a, b, c or d. It is hoped that these additional results can be reported during the course of this conference.

The shift in eigenvalues of acetylene (without extra hydrogens) when this molecule approaches the nickel surface is presented in Fig. 3. All of the levels except the $4a_1$ shift downward when height h becomes small. The $4a_1$ state which shifts more slowly than the

FIGURE 1.

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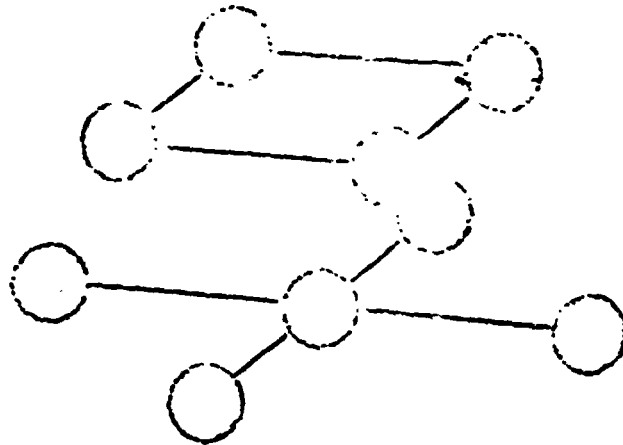
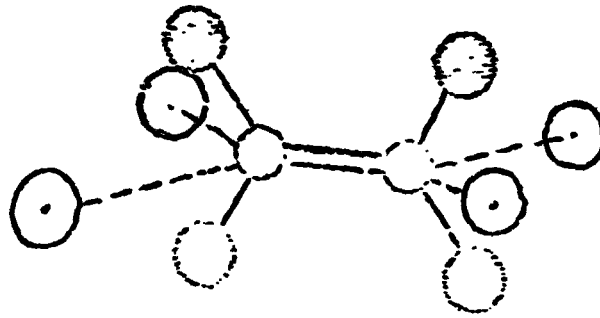


FIGURE 2. Arrangement A

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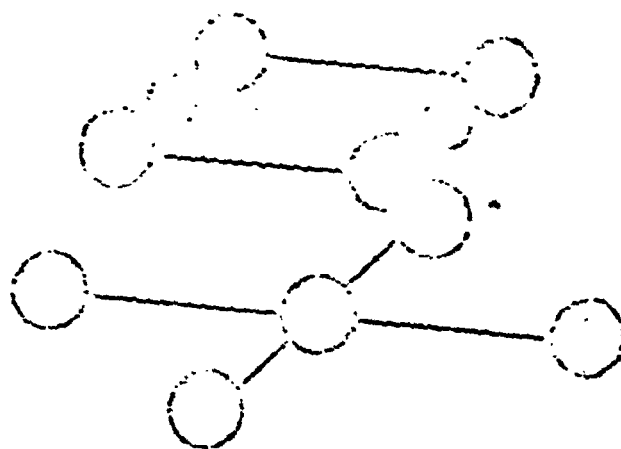
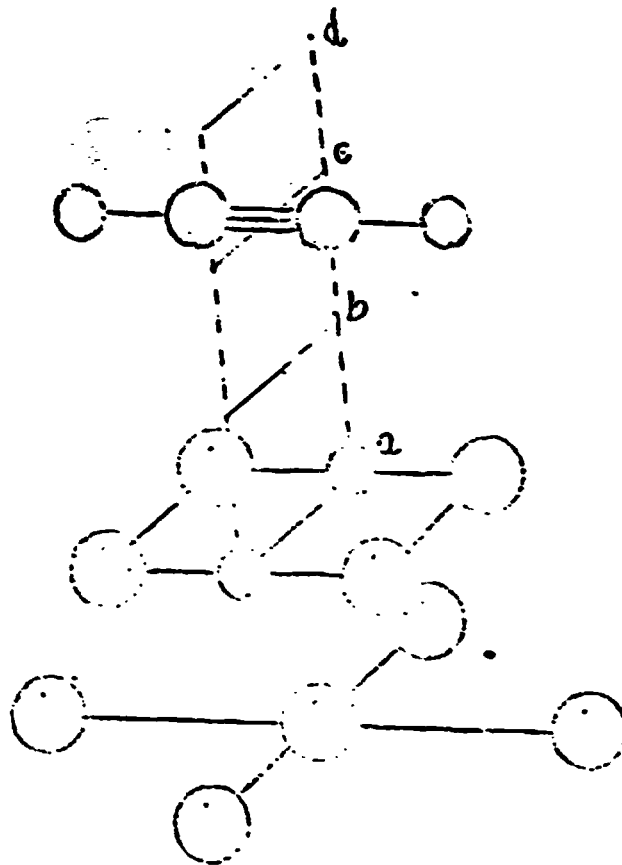
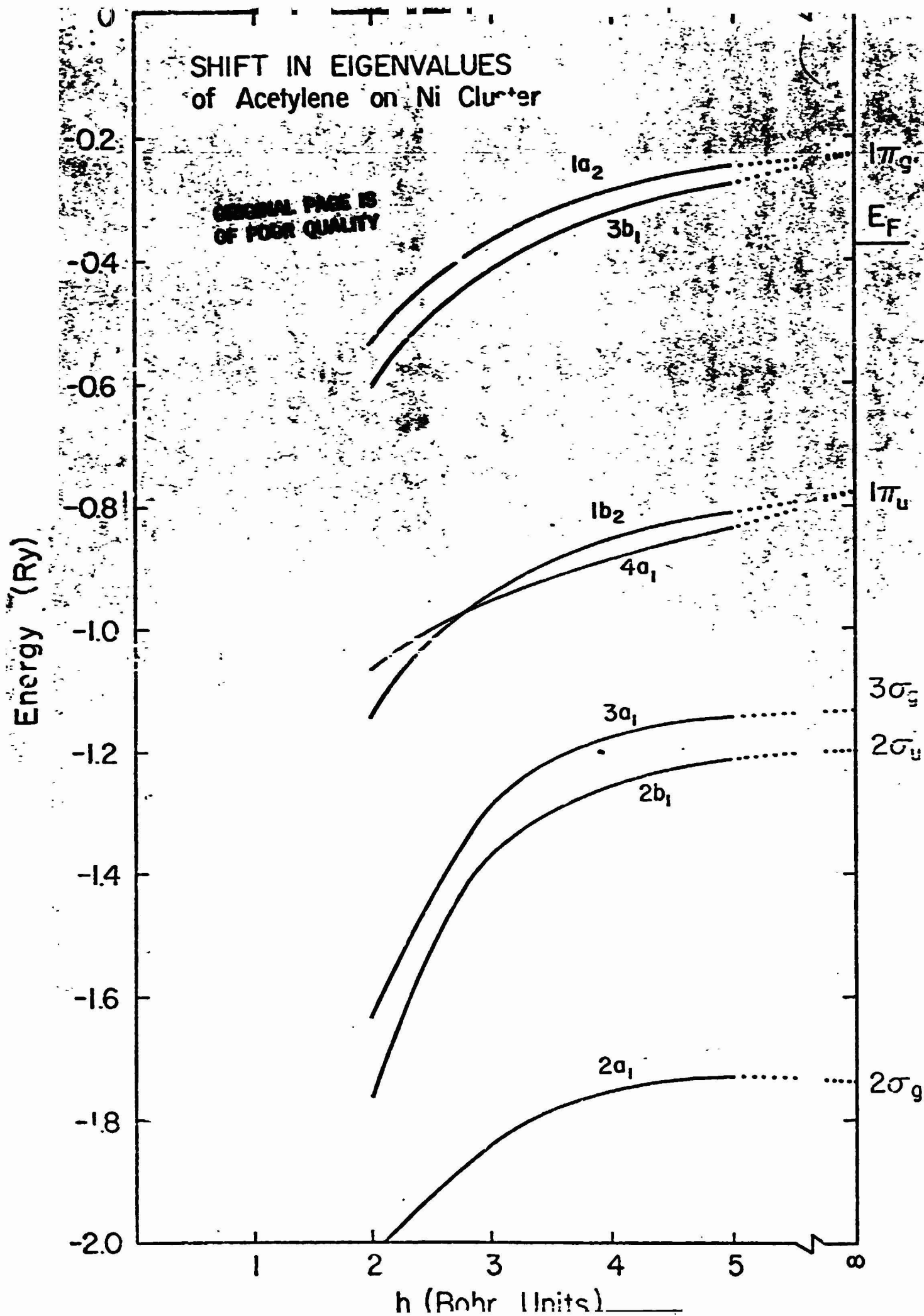


FIGURE 2. Arrangement B

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SHIFT IN EIGENVALUES of Acetylene on Ni Cluster



$1b_2$ and crosses it at about 2 Bohr units. This state characterizes the π bonding state of the two carbon atoms and the orbital is derived mainly from carbon $2p\pi$ orbitals states. As h becomes smaller, the amount of the carbon $2s$ function in this state orbital increases and polarization of $2p\pi$ orbitals becomes stronger. Electrostatic repulsion causes the latter charge to become localized into the region halfway between carbon atoms. In such a case, this state has a tendency to reduce the influence which the potential of the nickel atoms exerts.

The results of population analysis presented in Table 1 for free C_2H_2 are compared with values obtained in earlier calculations and the changes with h are shown in Fig. 4. The net charge on carbon atoms decreases while that on hydrogen increases rapidly when the molecule approaches to within about 3 Bohr units of the nickels. The population in the C-H bond slightly increases.

ETHYLENE ON Ni

We have calculated for arrangements A and B of ethylene as it approaches the (001) Ni plane. The various symmetrized orbitals used in these Perturbed Molecular Calculations compatible with the two arrangements are presented in Table 2. A free molecule of C_2H_4 would have C_{2v} symmetry whereas acetylene can be described as $D_{\infty h}$. However, the perturbing potential from the nickel atoms in the overall cluster reduce the pertinent symmetry to C_{2v} when h is small. For convenience both labels are given in Table 2.

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Table 1.

Eigenvalues and Populations of Acetylene
For the Free Molecule

	HF (1)	HF (2)	HFS (3)
Eigenvalue (HR)			
2 σ_g	-1.041	-1.004	-0.870
2 σ_u	-0.764	-0.751	-0.599
3 σ_g	-0.682	-0.656	-0.567
1 σ_u	-0.413	-0.405	-0.386
1 Π_g	+0.176	+0.305	-0.116
3 σ_u	+0.236	+0.475	+0.047
Populations			
H 1s	0.741	0.812	0.509
C 1s	1.999	1.997	1.999
2s	1.208	1.105	1.196
2p _{x,y}	1.000	1.000	1.000
2p _z	1.051	1.086	1.296
(C-H) σ_g	0.382		0.357
σ_u	0.370		0.319
total	0.752		0.676

(1) Hartree-Fock: L. C. Snyder and H. Sasch, "Molecular Wave Functions and Properties," John Wiley & Sons, 1972.

(2) Hartree-Fock: W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc. 88, 2384 (1966).

(3) Non-self-consistent Hartree-Fock-Slater: this work.

POPULATION CHANGES
IN ACETYLENE
(near Ni Cluster)

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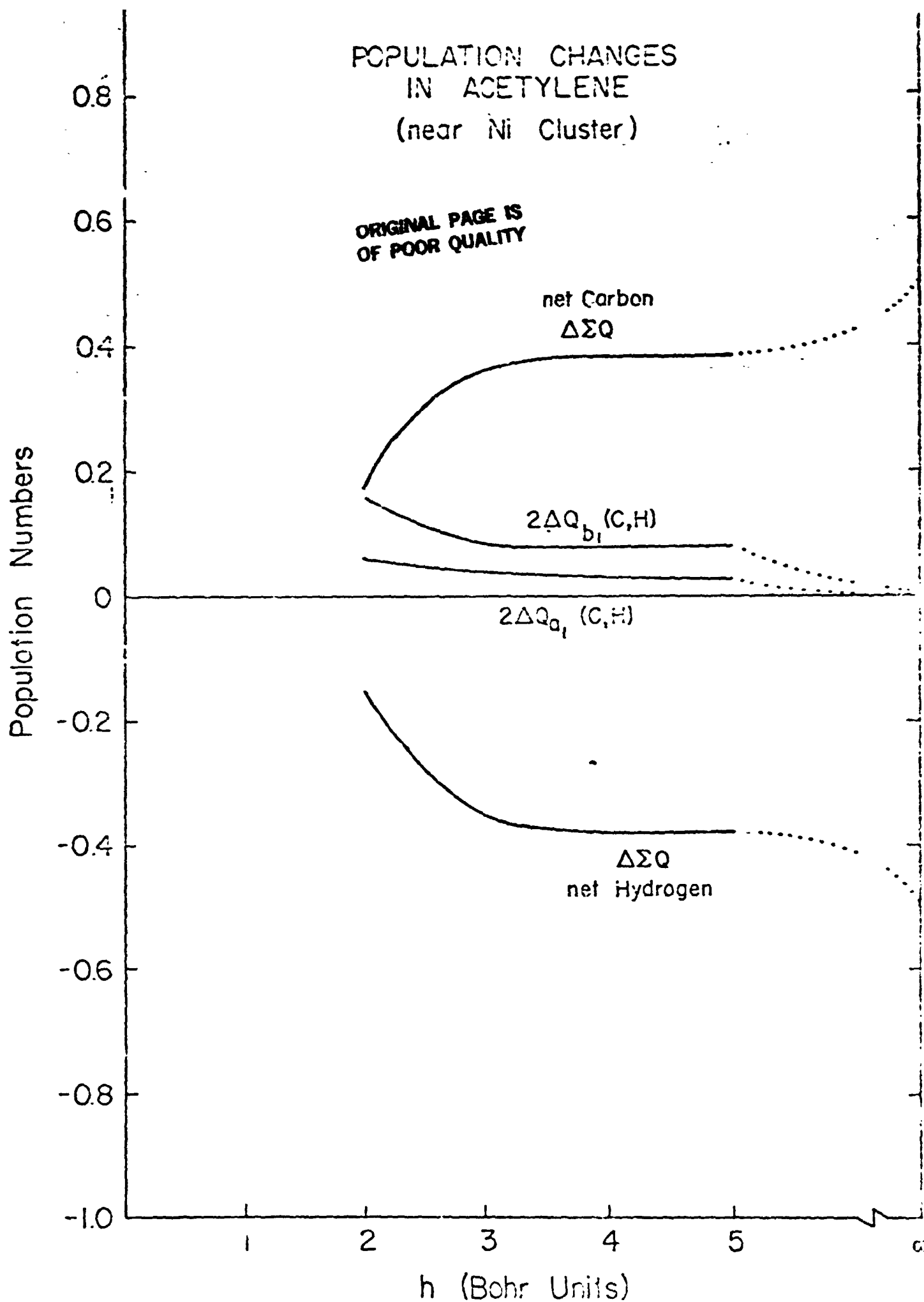


Table 2.

Symmetrized Orbitals for Ethylene with Hydrogen Arrangements

C _{2v}	D _{2h}	Parallel		Perpendicular *		Orbital Shape
		Orbital Combination		Combination	D _{∞h}	
a ₁	a _g	$\phi_B(1) + \phi_B(2)$		same		
a ₁	b _{1u}	$\phi(1)(p_z) + \phi(2)(p_z)$		same	b _{2u}	
a ₁	a _g	$\phi(1)(p_x) - \phi(2)(p_x)$		same		
a ₁	a _g	$\phi_B(3) + \phi_B(4) + \phi_B(5) + \phi_B(6)$		$\phi_B(3) + \phi_B(5)$ or $\phi_B(4) + \phi_B(6)$	a _g b _{2u}	
a ₂	b _{1g}	$\phi(1)(p_y) - \phi(2)(p_y)$		same	b _{2g}	
a ₂	b _{1g}	$\phi_B(3) - \phi_B(4) - \phi_B(5) + \phi_B(6)$		not applicable	-	
b ₁	b _{3u}	$\phi_H(1) - \phi_H(2)$		same	b _{3u}	
b ₁	b _{2g}	$\phi(1)(p_z) - \phi(2)(p_z)$		same	b _{1g}	
b ₁	b _{3u}	$\phi(1)(p_x) + \phi(2)(p_x)$		same		
b ₁	b _{3u}	$\phi_B(3) + \phi_B(4) - \phi_B(5) - \phi_B(6)$		$\phi_B(3) - \phi_B(5)$ or $\phi_B(4) - \phi_B(6)$	b _{3u} b _{1g}	
b ₂	b _{2u}	$\phi(1)(p_y) + \phi(2)(p_y)$		same	b _{2u}	
b ₂	b _{2u}	$\phi_B(3) - \phi_B(4) + \phi_B(5) - \phi_B(6)$		not applicable	-	

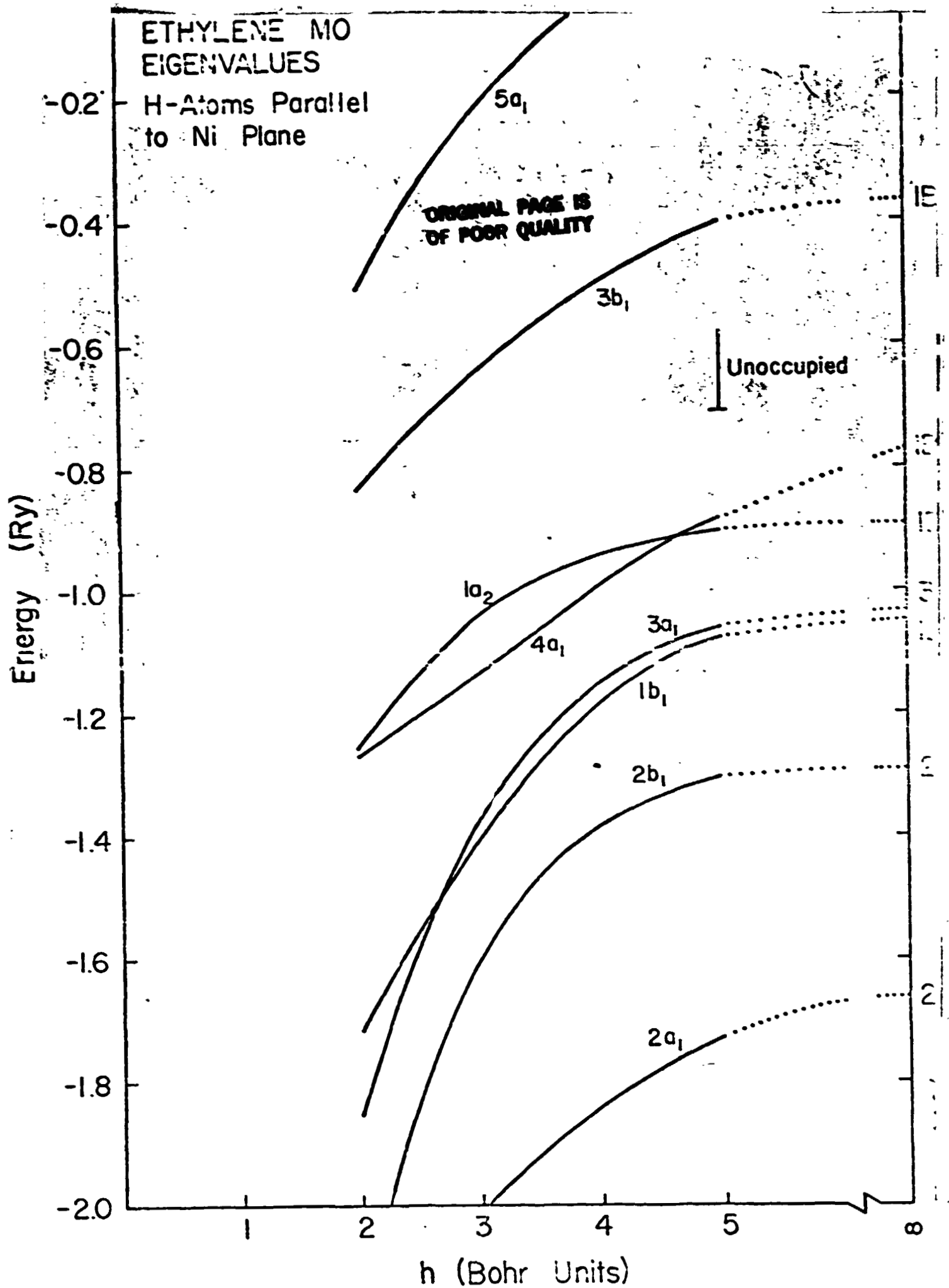
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*These differ by a $\frac{\pi}{2}$ rotation of the Z axis of the molecule. Those orbitals marked "parallel" are for the Z axis of the molecule parallel to the Y axis of the cluster. Those in the right hand side of the table are for its Z axis parallel to [01], as shown in Fig. 1. Certain symmetry labels are, therefore, interchanged.

Shifts of levels with h for the parallel orientation are shown in Fig. 5. The $4a_1$ level begins to drift downward at relatively large h and it crosses the $1a_2$ level at about 5 Bohr. The latter is constructed mainly of carbon $2p_z$ orbitals assuming that the z axis is perpendicular to the nickel surface.

The present population numbers computed for the free ethylene molecule are compared in Table 3 with those found in earlier calculations. Fig. 6 illustrates the related changes in population numbers as h decreases. The charge on carbon atoms decreases slightly to a minimum at $h \approx 3$ Bohr and then increases. It is interesting to notice that the change in C-H bond, namely $Q_{\text{total}}(\text{C-H})$, increases initially and decreases at small h . It becomes smaller than that for the free molecule when distance of approaching h is smaller than about 3 Bohr.

In this arrangement, where the two lower hydrogen atoms (H_2) approach collinearly and parallel to the (001) direction, there can be very little separation, s_{ij} , between these two hydrogens and two of the nickel atoms. The carbon atoms and the other hydrogen atoms are farther away from the surface. We now see quite different behavior from the parallel case. Fig. 7 illustrates the rather complicated shifts in the eigenvalues. The orbital functions of the $3a_1$, $2b_1$, $5a_1$, and $4b_1$ levels include relatively large amounts of the lower hydrogen atoms $1s$ as well as of carbon $2p_z$ functions. Thus these levels start to fall rapidly at the rather large height h of about 6 Bohr while remaining levels only begin to shift at about 5 Bohr.



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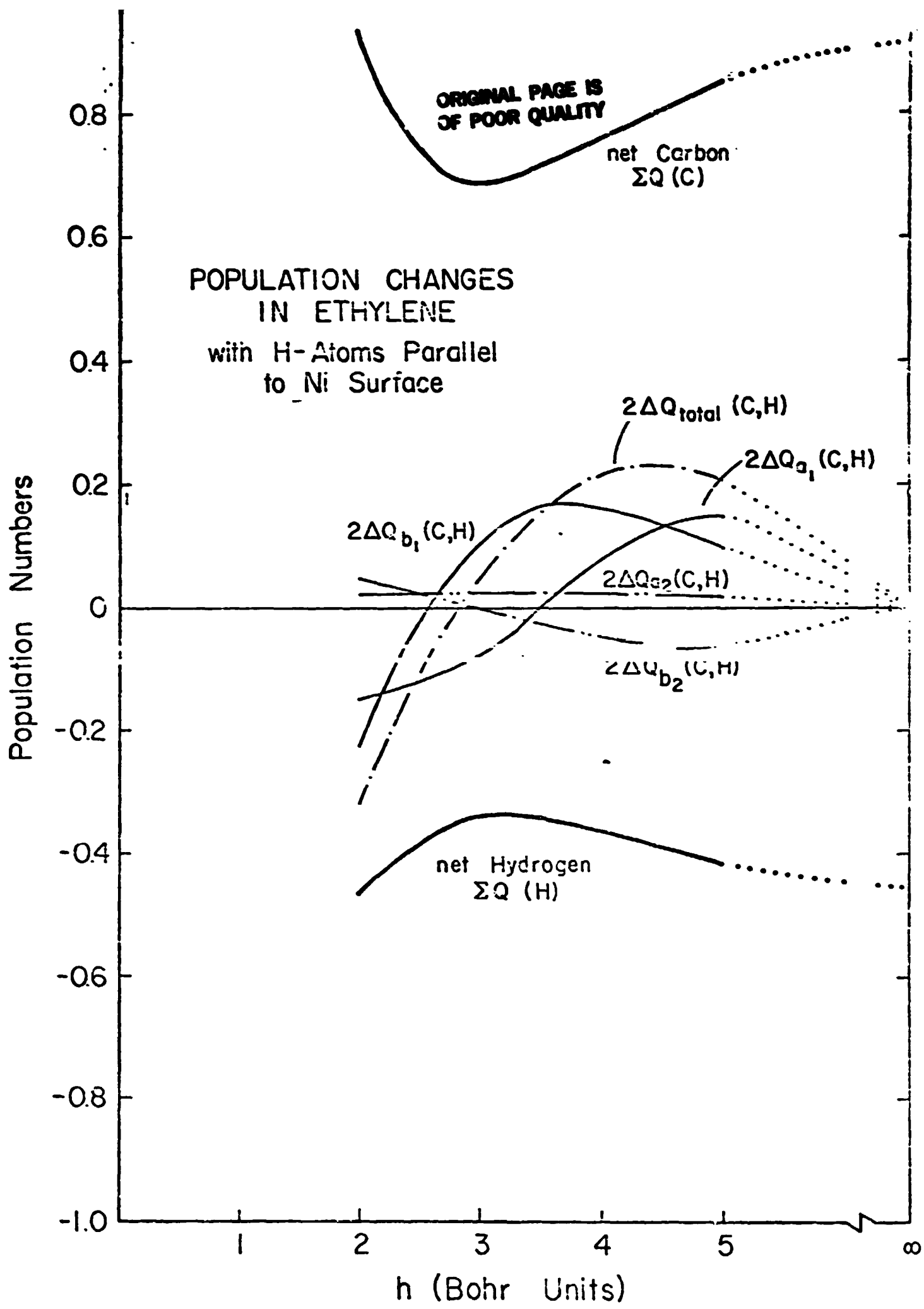
Table 3.

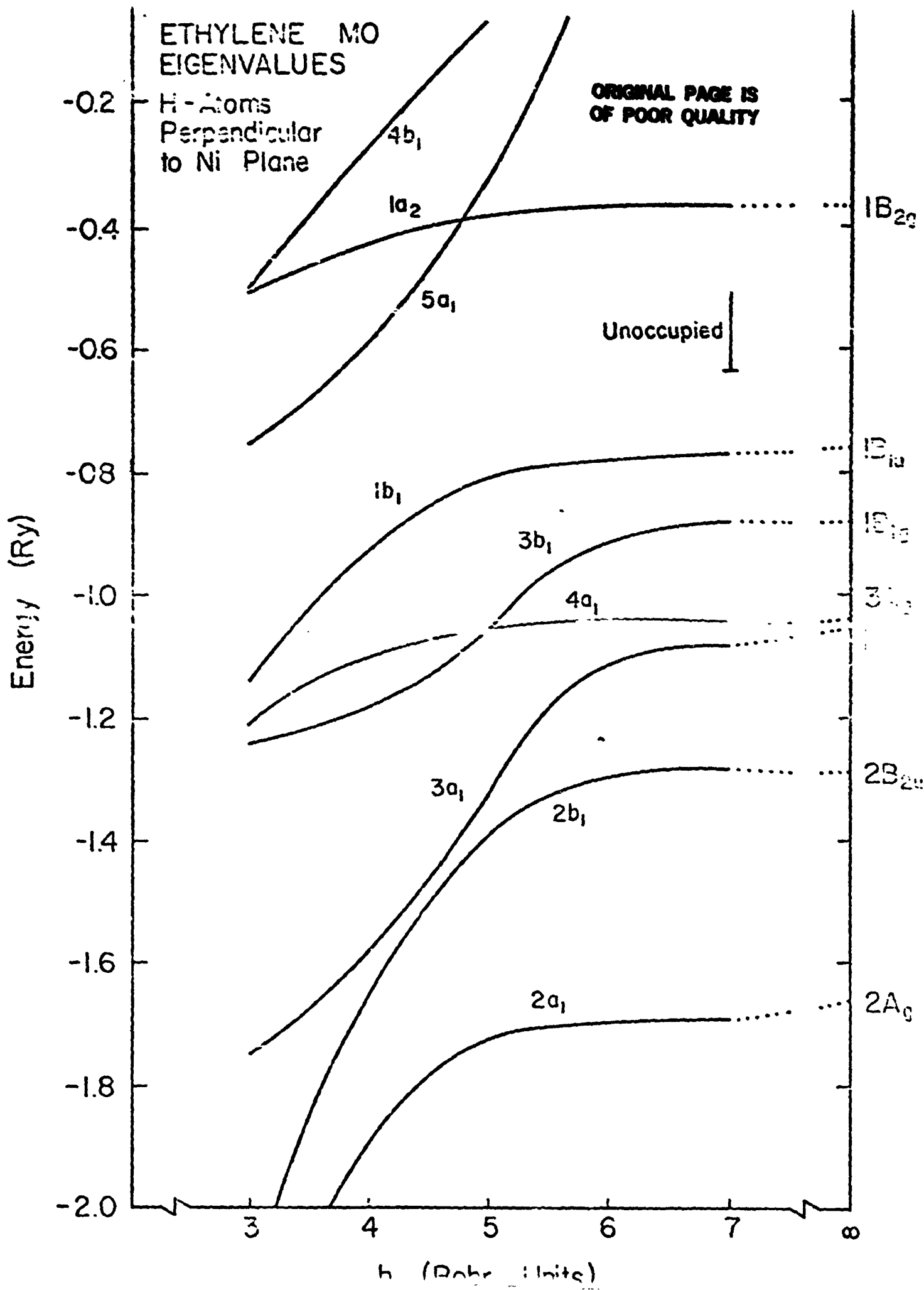
Eigenvalues and Populations of Ethylene
For the Free Molecule

	HF (1)	HF (2)	EHT (3)	HFS (4)	HFS (5)
Eigenvalue (E_R)					
2a _g	-1.038	-1.014	-0.992	-0.659	-0.829
2b _{3u}	-0.791	-0.782	-0.758	-0.486	-0.647
1b _{2u}	-0.646	-0.643	-0.596	-0.376	-0.526
3a _g	-0.585	-0.561	-0.531	-0.307	-0.520
1b _{1g}	-0.504	-0.506	-0.506	-0.264	-0.447
1b _{1u}	-0.375	-0.370	-0.486	-0.188	-0.382
1b _{2g}	+0.145	+0.242			-0.185
Population					
H 1s	0.525	0.860	0.881	0.781	0.540
C 1s	1.990	1.996			2.003
2s	1.269	1.197	1.183	1.285	1.451
2p _x	1.097	1.072	1.106	1.072	1.066
2p _y	1.000	1.000	0.962	1.000	1.000
2p _z	0.983	1.013	1.100	1.013	1.403
(C-H) total	0.719		0.813	0.792	1.147

- (1) Hartree-Fock: L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties," John Wiley & Sons, 1972.
- (2) Hartree-Fock: W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc. 88, 2384 (1966).
- (3) Extended Hückel model: R. Hoffmann, J. Chem. Phys. 39, 1397 (1963).
- (4) Self-consistent Hartree-Fock-Slater: E. J. Baerends and P. Ros, Chem. Phys. 2, 52 (1973).
- (5) Non-self-consistent Hartree-Fock-Slater: this work.

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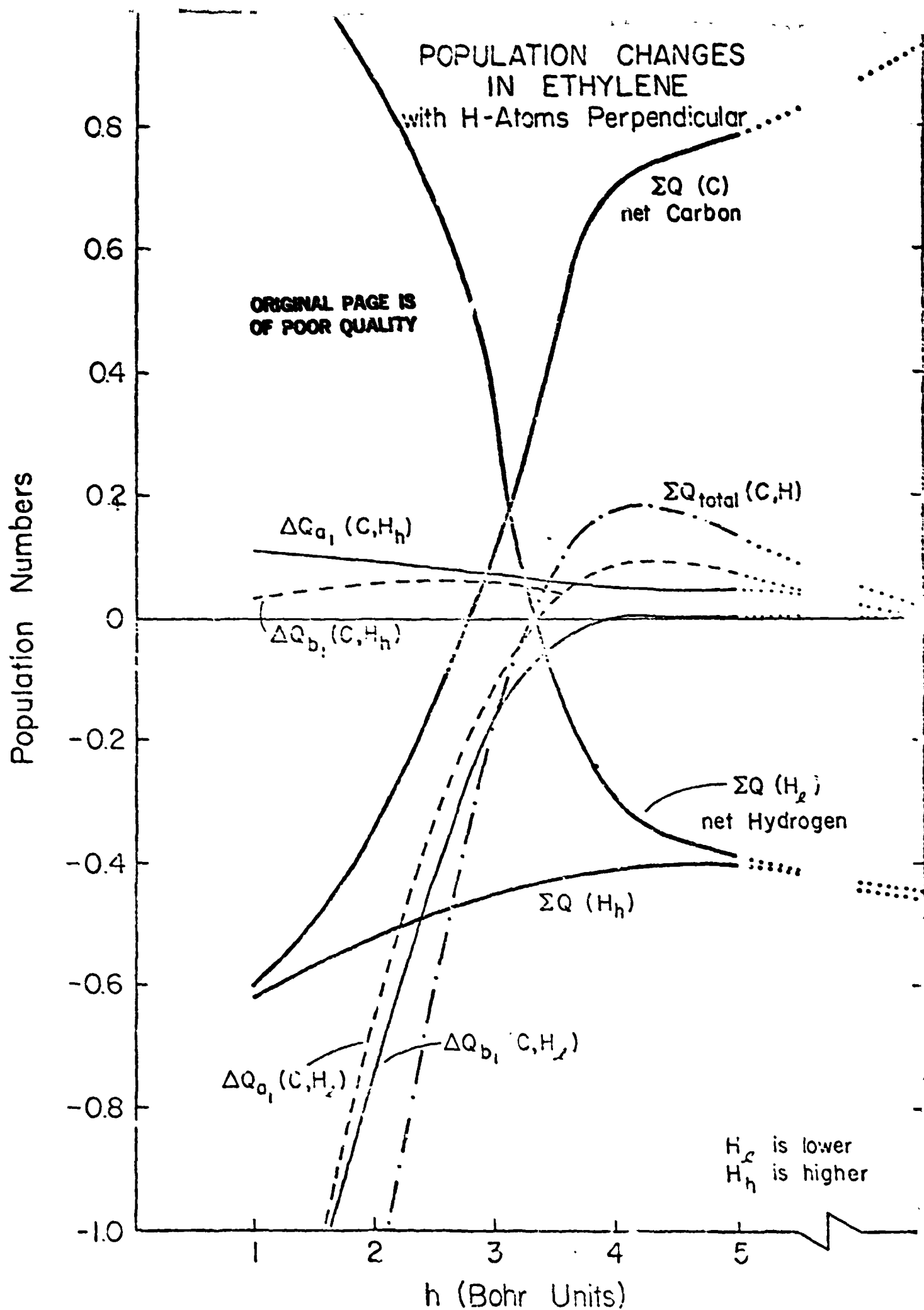


Dramatic changes in population numbers begin to occur when h becomes about 6 Bohr, as shown in Fig. 8. The charge on the lower two hydrogen atoms (H_L) increases rapidly, and while the population of the carbon atoms and in the carbon-lower hydrogen bonds decreases. It is reasonable that population number of the upper two hydrogens (H_U) and in carbon-higher hydrogen bonds do not change very much; the former decreases and the latter increases slightly.

DISCUSSION

So far we have not calculated transition probabilities. There are sufficient problems associated with performing accurate self-consistent charge calculations and we are not convinced of the reliability of our total energy calculations. The estimation of transition probabilities will not be undertaken until these other questions are explored and the best procedure settled on.

There are several broad peaks which are found in UPS and INS data for oxygen and for carbon monoxide⁽⁷⁾ adsorbed on nickel. They differ in intensity from one adsorbate to another even though they are located in approximately the same energy region several volts below the Fermi level. It is reasonable to expect that the probability for photoionization and the transition probability between electron levels will vary from level to level and from adsorbate to adsorbate.



The present perturbed molecular calculations as well as those where we have done to attain a self-consistent charge yield only discrete E values. They are discrete since only a small number of atoms are involved. However, the UPS and INS data are collected using essentially bulk metallic specimens which are covered with the adsorbate. Even if the changes in electronic charge density occur in only the first few layers of metal [that this number is large is more likely if the truncating plane is a high index (hkl) plane], the substrate-adsorbate complex will have a two dimensional periodicity. Since the MO states near the Fermi level are derived principally from atomic s and p states, and these correspond to zero momentum ($k = 0$) or Γ states in the band picture. The consequence of including a two dimensional lattice (perhaps three or four atomic layers thick) will be that there will be a spread and an upward trend of the $E(k)$ in the two dimensional Brillouin zone. Thus the fact that on our self-consistent calculations for O on a Ni cluster and S on a Ni cluster now lead to energy values which are lower than the average position of the UPS and INS experimental bands, should not be viewed as evidence that there is a real defect of the present method.

We are currently working to remedy this fault, but no results are available. Had the UPS and INS results been obtained for adsorption on a supported catalyst, then some questions might legitimately be asked about the reliability of the present method.

As noted above, the photoionization process must be carefully handled. If the metallic clusters are electrically isolated when supported on the Al_2O_3 and amorphous SiO_2 , then the electron ejected by the photon must come from the nickel atoms in the proximity of the adsorbate. This in itself would slightly modify the energy levels in the adsorbate even if the nickel atom were not contiguous to the adsorbed molecule.

At the moment, in order to obtain reasonable agreement between these UPS and INS bands we find that either O or S atoms must have an excess charge of from 0.3 to 0.5 electrons, to yield energy levels (calculated in accordance with Slater's transition state theory) which are in the right energy range, i.e. positive enough. The source of this excess charge is not specified. It is tacitly assumed that it was initially obtained from the bulk nickel. The formation of negative oxygen and sulphur is unreasonable since considerable charge transfer must occur to make crystalline NiO or NiS reaction layers. The present calculations only relate to the "necessary" precursor, a chemisorbed layer. The UPS and INS experiments have been done using a complete 1×1 centered $(100)Ni-c(2 \times 2)$; this arrangement is verified by LEED measurement.⁽³²⁾ In order for the photoemission to be more strongly influenced by the adsorbate than the bulk substrate, it appears very likely to the authors that the electrons involved in the ionization process orbitals are localized in the nickel-adsorbate bonds.

One problem, then, of making a detailed comparison with Eastman's⁽³³⁾ photoionization data is how to decide just where to remove one-half of an electron from distributed orbitals in a molecular cluster. Johnson⁽¹⁵⁾ has used such transition state calculations for his (MSC-X₂) study of molecular clusters with rather good success in treating the excitation spectra of molecules. So the problem may not be serious but merits some further attention.

Some years ago in connection with a study of the binding energy of an electron in a free atom, Liberman and Waber⁽³⁴⁾ showed that Koopman's theory is not valid except in the sudden approximation. This is certainly not true in a Hartree-Fock-Slater approximation but is also not exactly true in a Hartree-Fock case. The measured binding energy is obtained for the adiabatic approximation, i.e. rearrangement of inner electron occurs. After detailed comparison of non-relativistic Hartree-Fock total E_T for Z electrons and for $Z-1$ electrons, the removal energy was found by Wood⁽³⁵⁾ to be very close to half way between the eigenvalue (for a certain n_l level) calculated for q_{n_l} and recalculated self-consistently for $q_{n_l}-1$ electrons. Careful analysis by Slater⁽⁴⁾ showed that no serious difficulty arises if one assumes fractional occupation numbers for q_{n_l} in deriving the set of coupled differential using the Rayleigh-Ritz Variational principle. He proposed a hypothetical transition state with one-half of the electrons in the initial state and one-half in the final state. This has been subjected to other tests and found to yield very

good agreement for atoms. It is the authors' opinion that the details of using it for molecules are not as well studied.

CONCLUSION

Calculation for acetylene and ethylene molecules perturbed by the potential from nine atoms of a (100) nickel surface have been carried out to study the shifts in the eigenvalue and population number of these molecules when they approach the surface. From the present population analysis it is found that populations in C-H bonds and in carbon $2p_z$ orbitals increase slightly when acetylene approaches the surface. Accordingly, we can expect that these changes in fact strengthen the C-H bonds and provide electrons to make C-Ni bonds. It is also reasonable to speculate that the "bound" molecule is similar to a free radical after such electron transfer and reactions with it may occur more readily.

In contrast, during the approach of ethylene, C-H bonds tend to lose charge at small values of h . This loss is stronger when the ethylene approaches with its molecular plane perpendicular to the surface. In this case, the population number in bonds between carbon and the lower two hydrogens (H_L) decreases rapidly while that of the upper carbon-hydrogen bonds slightly increases. This means that a dissociative adsorption into an acetylene plus two hydrogen atoms can be expected.

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CAPTIONS

- Fig. 1. Illustration of two arrangements of the hydrogen atoms in an ethylene molecule as it approaches a nine atom cluster of nickel atoms. The axis of quantization is Z axis which is parallel to $[001]$ direction of the cluster.
- Fig. 2. Possible locations of two hydrogen atoms as they approach an acetylene molecule oriented along the X axis. In arrangement A, the H-H line is also parallel to the X axis whereas in arrangement B, this line is parallel to Y.
- Fig. 3. Shift in eigenvalues of acetylene as it approaches the Ni cluster. The symmetry labels of the free molecule are presented on the right side at $h = \infty$.
- Fig. 4. Changes in the population numbers for acetylene as it approaches the Ni cluster.
- Fig. 5. Shift in MO eigenvalues for ethylene with its hydrogen atom on different Ni parallel to the Y direction of the cluster, i.e. dotted lines in Fig. 1.
- Fig. 6. Changes in population numbers for ethylene with the four hydrogen atoms parallel to Ni surface.
- Fig. 7. Ethylene MO eigenvalues for its hydrogen atoms being perpendicular to the Ni $[001]$ plane, solid circles in Fig. 1.
- Fig. 8. Population changes in ethylene with hydrogen atoms perpendicular to Ni surface, i.e. parallel to the $[001]$ direction.

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