

## Extended Hückel Calculations on the Chemisorption of Acetylene on Tungsten \*

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The chemisorption of acetylene on various faces of bcc tungsten, modelled by clusters of various sizes, has been studied by the Extended Hückel method. Relative binding energies on the various sites have been obtained, and the bonding modes of acetylene are discussed, also in comparison with experiment. It is concluded that, whenever possible, acetylene is *di- $\sigma$*  bonded to the surface, and *sp*<sup>2</sup> hybridization is considered likely in all cases.

**Key words:** Acetylene, chemisorption of  $\sim$  on tungsten

### 1. Introduction

Molecular orbital studies of chemisorption of organic molecules on heavy metals are rapidly growing in number and accuracy, especially in connection with the so-called cluster approach, in which the metal surface is represented by a finite number of atoms (see, for an account of these methods, Ref. [1]). While *ab initio* SCF-type calculations seem to be still out of the reach of present computational facilities, semiempirical methods have been widely used; we are at present engaged in the exploration of the capabilities of Extended Hückel Theory (EHT) [2] in the field (see Refs. [3–4] and references therein).

The W surface and the chemisorption of H [5], N [6], first-row diatomics [7] and CO [8] have been studied by EHT. On the experimental side, acetylene chemisorption on W has been studied by Electron Energy Loss Spectroscopy (ELS) [9–10]

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\* This paper is dedicated to Professor Hermann Hartmann on the occasion of his 65th birthday.

and UPS [11], as well as by a multi-technique approach [12]. We present in this paper our EHT results for the adsorption of acetylene on different sites of the (100), (110) and (111) W surfaces.

## 2. Calculations

We define a “surface plane”, the “acetylene plane”, and the distance  $R$  in the same way as in Ref. [3]; also, the back-bent conformation for the acetylene molecule, as defined in Ref. [3], is adopted in all calculations. Figure 1 shows sketches that help in understanding all these definitions, as well as the shapes of the clusters. As usual, the size of the cluster is a compromise between the need of a fair representation of the surface properties (that requires a number of atoms as large as possible) and the need to keep the amount of computing time at a reasonable level.

The problem of large charge shifts between atoms in the clusters, as computed by EHT, was recognized as an important one in the discussion of bonding between surface and adsorbate [5–7], and was solved [5] in an empirical way by adjustments of the  $5d$  and  $6s$  Valence Shell Ionization Potentials (VSIP's) to be used in the calculation of EHT matrix elements according to the Wolfsberg–Helmholtz formula. In our calculations, the values for these parameters that were obtained in Ref. [5] have been used for the clusters representing the (100) face (for which they were originally derived) and also for the clusters modelling the (110) face, that have a similar shape. Newly adjusted parameters were obtained for the (111) clusters. The goal of these adjustments is always the smoothing down of charge differences between atoms in a cluster; Table 1 shows the values adopted for the VSIP's in each case, together with the maximum charge difference between two atoms in the same cluster, which is a measure of the success of the adjustment. Figure 2 shows some detail on the final calculated electronic structures of the clusters.

Another important point concerns the choice of the basis set for the metal atoms. The concept of “valence” orbitals being somewhat looser in metals than, say, in carbon atoms, one is left for W with a choice among combinations of  $5p$ ,  $5d$ ,  $6s$  and  $6p$  orbitals. The inclusion of  $5d$  orbitals being obvious, that of the  $6s$  orbital seems very reasonable; the essential role of  $5p$  orbitals seems to be that of providing a repulsion between surface and adsorbate at small separation [5], while  $6p$  orbitals are possibly important in enhancing surface-adsorbate bonding effects [3]. On the other hand, the repulsion due to inner  $5p$  orbitals has been found to be well represented by an empirical formula [5]

$$E(\text{rep}) = \sum_{i,j} A e^{-Br_{ij}},$$

the summation being taken over all the cluster–adsorbate  $W \cdots X$  pairs ( $X = C$  or  $H$ ). Our present choice of the basis set includes  $5d$  and  $6s$  orbitals, plus the repulsion term calculated by the above formula; the observation [5] that the summation over pairwise repulsive terms approaches very well the overall repulsive

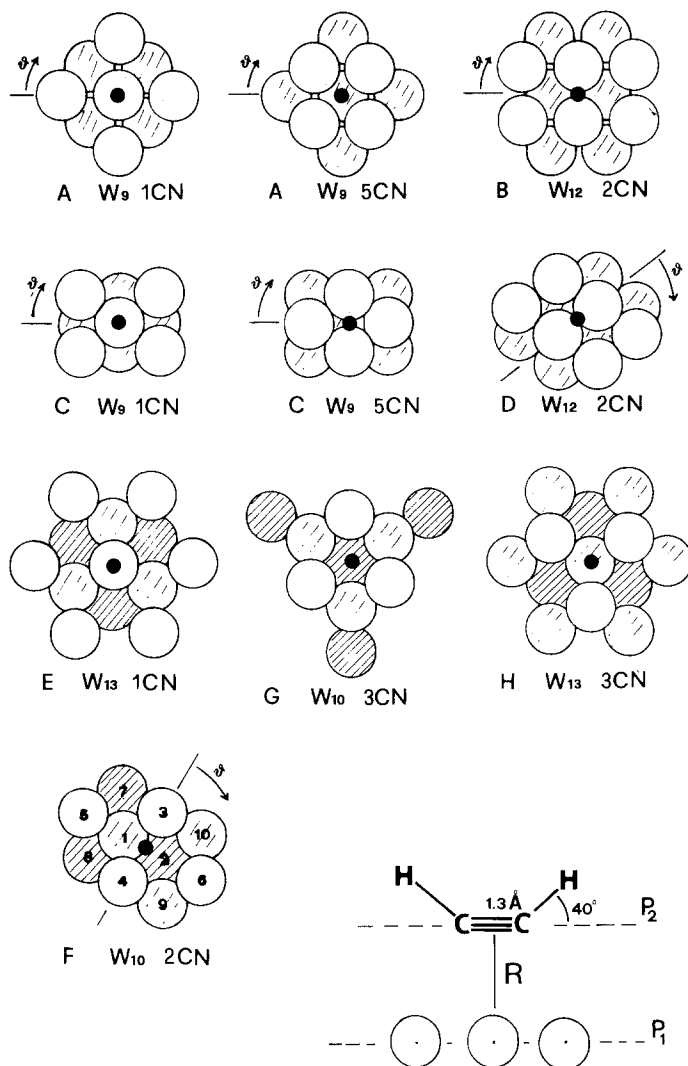


Fig. 1. The clusters used in the calculations: A-B, (100); C-D, (110); E-H, (111).  $P_1$  is the trace of the surface plane (the plane that contains the nuclei of the W atoms of the first layer in a cluster);  $P_2$  is the trace of the acetylene plane (that contains the C atoms and is parallel to the surface plane).  $R$  is the distance between  $P_1$  and  $P_2$ .  $\theta$  is the angle of rotation of the acetylene molecule in the acetylene plane. The black dots are the projections of the  $C \equiv C$  bond midpoint onto the surface plane

effect has been confirmed by our calculations. We used the values:

$$A(W \cdots C) = 474.44 \quad B(W \cdots C) = 3.6266$$

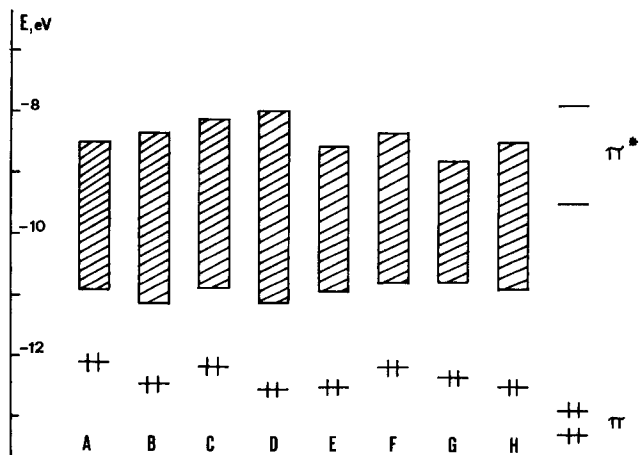
$$A(W \cdots H) = 139.0 \quad B(W \cdots H) = 3.584$$

(to give energies in eV), obtained by a procedure strictly similar to that outlined in Ref. [5] for  $W \cdots C$ , and taken from Ref. [5] for  $W \cdots H$ .

**Table 1.** VSIP's (eV) and Slater exponents used in the calculations

		VSIP	Exponent	
H	1s	-13.6	1.3	
C	2s	-21.4	1.625	
	2p	-11.4	1.625	
W	5p	-46.07	4.91	
W, VSIP's <sup>a</sup>				
Cluster		5d	6s	max $\Delta q^b$
A <sup>c</sup>	edge	-8.76	-7.76	0.1
	corner	-8.52	-7.52	
	central	-9.0	-8.0	
B <sup>c</sup>	central	-9.0	-8.0	0.1
	external	-8.68	-7.68	
C		see cluster A		$\approx 1.0$
D		see cluster B		0.52
E	inner 7	-9.0	-8.0	0.1
	outer 6	-8.65	-7.65	
F <sup>d</sup>	1-2	-9.0	-8.0	0.1
	3-4, 9-10	-8.75	-7.75	
	5	-8.72	-7.72	
	6	-8.87	-7.87	
	7-8	-8.5	-7.5	
G	inner 7	-9.0	-8.0	0.1
	outer 3	-8.82	-7.82	
H	inner 7	-9.0	-8.0	0.1
	outer 6	-8.55	-7.55	

<sup>a</sup> 5d Slater exponent 2.4; 6s exponent 1.4. <sup>b</sup> Maximum charge difference between atoms in the cluster, A-D; between atoms in the same layer, E-H. <sup>c</sup> From Ref. [5]. <sup>d</sup> See Fig. 1 for numbering.



**Fig. 2.** The occupied MO's and *d*-bands (dashed areas) for the clusters in Fig. 1; on the right are shown the occupied  $\pi$  and the unoccupied  $\pi^*$  levels of back-bent acetylene

### 3. Results

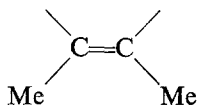
The binding energy is as usual calculated as the difference between the sum of the energies of the separate fragments (cluster and acetylene molecule) and the energy of the “surface molecule” that is formed when the two are brought into contact. It is an intrinsic shortcoming of simple MO methods that the binding energy converges to wrong values at infinite separation, as unrealistic ionic species are formed. This, however, may have little effect on comparisons between relative energies for various sites on various clusters, provided these have similar electronic structures (see Fig. 2). Figure 3 collects some binding energy curves for the three faces. Table 2 collects some numerical values for binding energies and distances from the clusters, as derived from inspection of the minima in Fig. 3, and thus necessarily approximate. From these, the following order of stability is obtained: on (100),  $2CN > 1CN > 5CN$ ; on (110),  $2CN > 5CN \approx 1CN$ ; on (111),  $1CN > 2CN > 3CN$ . Therefore, on (100) and (110) each C atom is sigma-bonded to a W atom, while on (111), where the W–W distances are too large to allow this, acetylene is chemisorbed on top of a single W atom.

### 4. Discussion

The electronic structures of the clusters (Fig. 2) show that the filled *d*-band width is a function of the number of atoms in the cluster and of the distance between metal atoms, in the sense that a larger number of atoms in the cluster or a more tightly packed cluster produce a larger interaction and hence a larger band width. The smaller band width is thus exhibited by the ten-atoms (111) cluster G (about 2 eV), while the largest one belongs to the 12-atoms (110) cluster D ( $\approx 3$  eV). The comparison with the observed filled *d*-band width is satisfactory (see the discussion of similar results in Ref. [7]).

The charge-smoothing procedures employed have been successful for clusters E–H; Table 1 shows that the charge differences between atoms in the same layer never exceeded 0.1 electrons. The optimized parameters [5] for clusters A–B were transferred to the similar clusters C–D, where of course larger charge differences were obtained. It may be pointed out that, although uniform charge distributions may be desirable from the standpoint of the reproduction of the properties of bulk metal, it is almost certain that, in actual catalysts, where small metal particles are involved, these particles may differ considerably from bulk metal in electronic structure, and in particular the effect of anomalous boundary conditions may be important, as exemplified for instance by the anomalous catalytic properties of stepped surfaces [13].

The results in Table 2 lend themselves to some generalizations concerning trends in the chemisorption of acetylene and small fragments on W. It is easily seen that, whenever possible, acetylene tends to adsorb in a *di*- $\sigma$  mode:



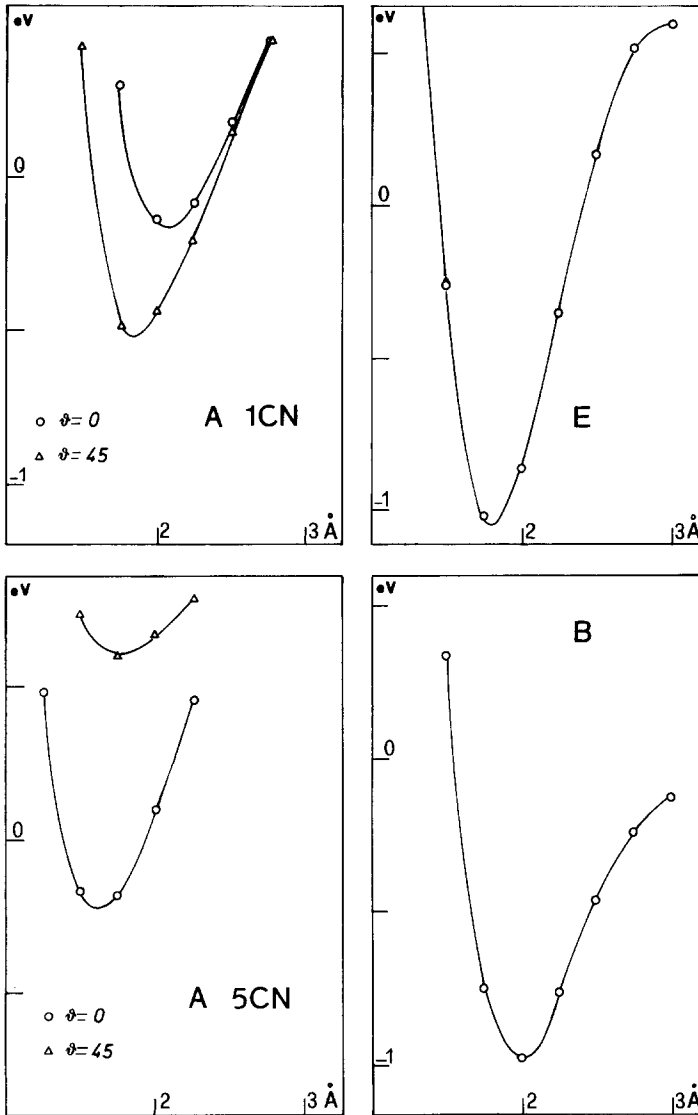


Fig. 3. Binding energy curves for acetylene adsorption on W. The letters A–F refer to clusters shown in Fig. 1. The abscissa is in all cases the distance  $R$  (see Fig. 1). See Fig. 1 for the definition of angles  $\theta$ ; where no  $\theta$  value is shown, only one adsorption orientation is possible (see Table 2). Negative values of the binding energy indicate a stable surface molecule

This is confirmed by the high binding energy of sites such as 2CN, especially on the tightly packed (110) surface. This is consistent with the fact that CH groups, as well as C or H atoms, have very high binding energies on W as compared with the acetylene molecule; test calculations showed that CH and C chemisorb on top of a W atom with  $BE \approx 10$  eV. It is not surprising that, on the basis of adsorption energies only, highly dissociative modes of adsorption be favoured; this tendency

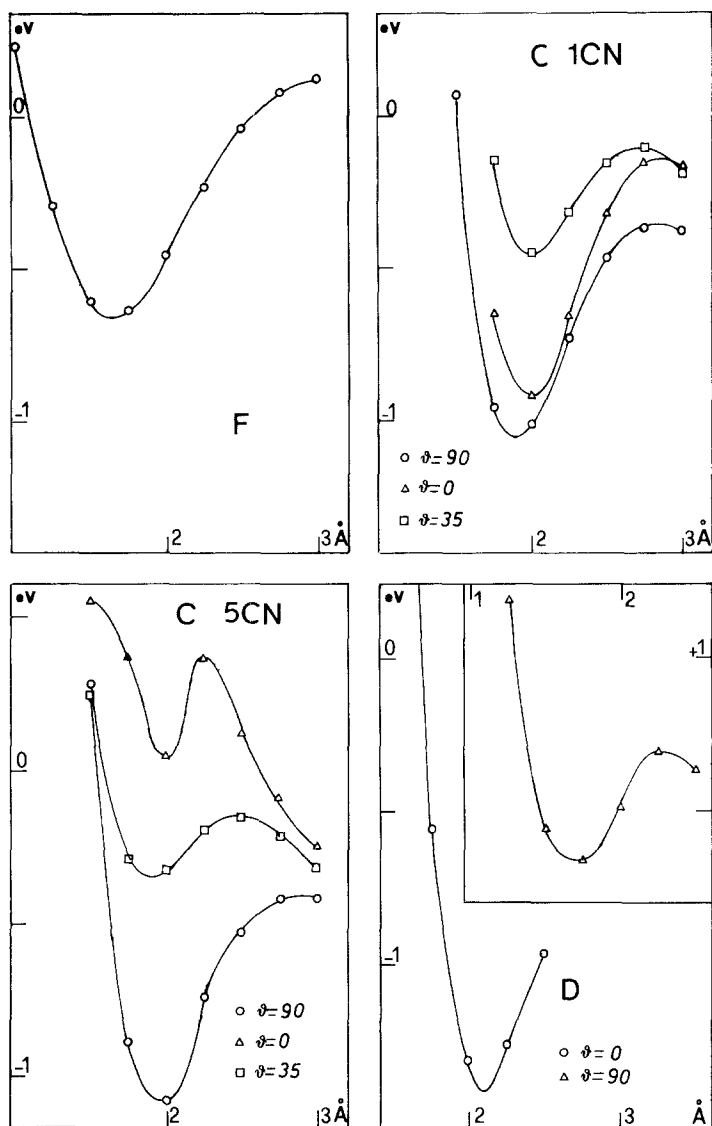


Fig. 3 (continued)

of adsorbates to place C atoms on top of metal atoms whenever possible was observed also in the case of acetylene [3] and other organic fragments [4] on Pt. Also consistent with these ideas is the fact that chemisorption at threefold sites, that seems to be preferred for acetylene on Pt on the basis of the analysis of LEED intensities [14], is always calculated to be unfavourable relative to other sites that offer W atoms nearer to the incoming C atoms. This point is probably rather sensitive to parameterization, and in particular to the spatial extension of the atomic orbitals of the metal.

The C-W distances for the more favourable adsorption sites range from 1.9 to

**Table 2.** Binding energies (eV), distances  $R$  (Å) between surface and acetylene plane, and carbon-tungsten distance (Å) at the points of minimum of the curves in Fig. 3

	$BE$	$R$	$R(C-W)$	cluster
(100)				
1CN $\theta = 0^\circ$	-0.17	2.1	2.2	A
$\theta = 45^\circ$	-0.53	1.8	1.9	A
5CN $\theta = 0^\circ$	-0.22	1.6	2.4	A
$\theta = 45^\circ$	+0.60	1.75	2.4	A
2CN $\theta = 0^\circ$	no adsorption			
$\theta = 90^\circ$	-0.98	2.0	2.2	B
(110)				
1CN $\theta = 0^\circ$	-0.92	2.0	2.1	C
$\theta = 35^\circ$	-0.45	2.0	2.1	C
$\theta = 90^\circ$	-1.06	1.9	2.0	C
5CN $\theta = 0^\circ$	+0.04	2.0	2.55	C
$\theta = 35^\circ$	-0.34	1.9	2.6	C
$\theta = 90^\circ$	-1.08	2.0	2.2	C
2CN $\theta = 0^\circ$	-1.41	2.1	2.2	D
$\theta = 90^\circ$	+0.34	1.7	2.4	D
(111)				
1CN any $\theta$	-1.05	1.8	1.9	E
2CN $\theta = 0^\circ$	-0.66	1.7	2.3	F
3CN any $\theta$	no adsorption			G, H

2.2 Å. The expected single bond length for a C-W molecule is about 2 Å (sum of the covalent radii); therefore, making use of the formula [15]

$$D(n) = D(1) - 0.71 \log(n)$$

in which  $D(n)$  is the observed bond length and  $D(1)$  is the single bond length,  $n$ , the bond order, ranges from 1.38 to 0.52. This is a reasonable result, although its implications on the C-C bond order are not immediate; it can be probably safely stated that it is not inconsistent with the picture of  $di-\sigma$  bonding that emerges from the analysis of the preferred adsorption sites. Also the calculated binding energies are in a quite reasonable range (22 to 33 kcal/mole). Further insight into the stability of the W-C bond could be gained by the desorption energy, obtained from the height of the barrier opposing to the stretching of the bond towards higher adsorbate-surface distances. Unfortunately, in our calculations this quantity is masked by the above mentioned convergence to ionic binding energies, due to the  $d$ -bands pouring electrons into the empty  $\pi^*$  MO of back-bent acetylene (see Fig. 2). It is however possible to obtain approximate stretching force constants from the curvature of the  $BE$  curves near the minima. The results of this analysis are shown in Table 3. This table also shows the values of the Mulliken [16] bond overlap populations for the acetylene C-C bond after chemisorption; an overlap population/bond order relationship was established using data for ethane, ethylene and acetylene, and this allowed the calculation of C-C bond orders for chemisorbed acetylene (Table 3). For the (100) and (111) surfaces the most stable site also has



**Table 3.** Stretching force constants,  $k$ , for acetylene-surface bonds at various sites (mdyn/Å); carbon-carbon bond overlap population (BOP) and bond orders (BO) for chemisorbed acetylene

		$k$	BO	BOP
(100)	1CN	0.79	1.8	1.15
	2CN	0.95	1.8	1.17
	5CN	0.64	1.8	1.15
(110)	1CN	0.81	1.8	1.16
	2CN	0.90	1.8	1.16
	5CN	1.60	1.95	1.28
(111)	1CN	1.27	1.95	1.25
	2CN	0.40	1.95	1.26

the largest stretching force constant; a very large force constant is obtained for (110) 5CN. C—C bond orders  $\approx 2$  are obtained everywhere, a result that is quite consistent with that of W—C bond orders of  $\approx 1$  for the preferred sites.

Comparisons with experimental results are very difficult to establish. The lack of ordering of adsorbed species for acetylene on W(100) [12] forbids extensive analysis by LEED, a technique very suitable to give structural details on chemisorbed species. On the other hand, ELS results indicate complex coverage-dependent chemisorption behaviour for acetylene on W [9–10]; and coverage is a variable that has never been taken into account in our calculations, although it would in principle be possible to study by MO methods not only adsorbate-surface interactions, but also adsorbate-adsorbate interactions, by using large clusters with many molecules of adsorbate. For associative chemisorption at high coverages, however,  $di-\sigma$  adsorption is proposed, and other arguments are in favour of  $sp^3$  hybridization for the C atoms on the W(110) surface [10]. UPS results for acetylene on W(100) [11] have been interpreted by qualitative arguments suggesting that the bonding site is directly over a W atom (1CN), and that the Dewar-Chartt  $\pi-d$  bonding model, originally proposed in the context of organometallic chemistry, applies also to surfaces; the C atoms of acetylene were considered to be  $sp^2$ -hybridized. Since we conclude that both on (100) and (110) acetylene is  $di-\sigma$  bonded with  $sp^2$  hybridization, while on (111) it is adsorbed over a single W atom, experimental results are in partial agreement with calculations; it should once more be emphasized, however, that both the interpretation of experimental results and the methods of calculation are still subject to continuous revision and critical examination.

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