

The convergence of the cluster model for the study of chemisorption: Be₃₆H

Paul S. Bagus, Henry F. Schaefer III, and Charles W. Bauschlicher Jr.

Citation: *The Journal of Chemical Physics* **78**, 1390 (1983); doi: 10.1063/1.444880

View online: <http://dx.doi.org/10.1063/1.444880>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/78/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Structure sensitivity and cluster size convergence for formate adsorption on copper surfaces: A DFT cluster model study](#)

J. Chem. Phys. **112**, 9562 (2000); 10.1063/1.481573

[Chemisorption of sulfur on nickel: A study of cluster convergence in the linear combination of Gaussian type orbitals local density functional approach](#)

J. Chem. Phys. **100**, 6578 (1994); 10.1063/1.467067

[Fourier transform ion cyclotron resonance studies of H₂ chemisorption on niobium cluster cations](#)

J. Chem. Phys. **88**, 5215 (1988); 10.1063/1.454596

[A proposal for the proper use of pseudopotentials in molecular orbital cluster model studies of chemisorption](#)

J. Chem. Phys. **81**, 3594 (1984); 10.1063/1.448107

[Model studies of chemisorption. Interaction between atomic hydrogen and beryllium clusters](#)

J. Chem. Phys. **62**, 4815 (1975); 10.1063/1.430391



The convergence of the cluster model for the study of chemisorption: Be_{36}H

Paul S. Bagus

IBM Research Laboratory, San Jose, California 95193

Henry F. Schaefer III

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Charles W. Bauschlicher, Jr.^{a)}

Polyatomics Research Institute, Mountain View, California 94043

(Received 13 August 1982; accepted 28 October 1982)

A three layer cluster (with 14, 8, and 14 atoms comprising the three layers) has been used to model the chemisorption of atomic hydrogen on the (0001) surface of beryllium. *Ab initio* molecular electronic structure theory was employed at the self-consistent field level with a minimum basis set (Be, 1s, 2s, 2p, and H 1s functions). The properties of the Be_{36} cluster are discussed in some detail, as is the adsorption of H on each of four different high-symmetry surface sites. Significant differences are reported for chemisorption on this model surface relative to the results obtained previously with a two-layer Be_{22} cluster. Changes in chemisorptive bond energies range from 0.2 to 9.7 kcal, while Be_nH distances change by 0.01 to 0.04 Å in going from Be_{22} to Be_{36} . It is concluded that some properties related to chemisorption converge reasonably rapid with respect to cluster size, e.g., bond distances, while others, e.g., dissociation energies, converge more slowly.

INTRODUCTION

A primary goal of recent research in surface chemistry and physics has been a molecular understanding of chemisorption and of the formation of the substrate-adsorbate bond.¹⁻⁴ For an analysis of the nature of the bond formed, it is useful to know such properties as the chemisorption energy, the binding site, the distance of the adsorbate above (or below) the surface, and the vibrational frequencies of the adsorbate-substrate complex. Thus, these properties have been extensively studied experimentally. Unfortunately, except for the measurement of the vibrations, the determination of the other properties is limited because of both experimental and interpretive problems. Because of the lack of understanding of many chemisorption problems, and the success of *ab initio* calculations for small molecules,⁵ we have engaged in a systematic theoretical study of the chemisorption of atomic hydrogen on the (0001) surface of beryllium⁶⁻⁸ to assess the possibility of using such techniques to investigate chemisorption. We have computed the chemisorption energy, bond length, and vibrational frequency for four high-symmetry sites as a function of increasing cluster size. This was done in order to determine which properties are local in nature and can reliably be computed with a cluster model and which properties cannot be easily determined from wave functions for finite clusters. Although this particular chemisorption problem has not been studied experimentally,⁹ the (0001) surface of metallic Be has been well characterized.¹⁰

When an *ab initio* cluster model is used, it is clearly

far easier to study convergence with respect to cluster size when the substrate atom is light, than when it is heavy. This follows simply because there are fewer electrons per atom, hence, *ab initio* calculations are computationally tractable for clusters with rather large numbers of substrate atoms. The H/Be (0001) system can indeed be studied experimentally⁹ and we hope experimental work will be forthcoming to permit tests of our theoretical predictions.

In previous papers,⁶⁻⁸ the approach adopted has been to model Be (0001) by clusters of beryllium atoms, with these clusters ranging in size from Be_3 to Be_{22} . The rough qualitative features of hydrogen atom chemisorption appear already in the Be_{13}H models. Among the four chemisorption sites considered, the H atom is least strongly bound at the on top, or directly overhead site. For the other three sites—bond midpoint, eclipsed [threefold site with a second layer Be atom below], and open [threefold site with no Be atom directly below]—the binding of H to the surface is considerably stronger. An analogous distinction between terminal and bridging hydrogens in organometallic chemistry has also been established¹¹ in recent years.

Some significant differences were found between the Be_{13}H and more recent⁸ Be_{22}H binding energies. For example, the open site chemisorptive bond energy increased from 39 to 55 kcal/mol between Be_{13}H and Be_{22}H . For Be_{22}H , the chemisorption energies for the strongest three sites are very similar. That, for the open site, is only 3.2 kcal/mol greater than that for the eclipsed site; that for the bond midpoint site lies between these two. For Be_{13}H , however, these sites were well separated; the binding of H in the eclipsed site is 21 kcal/mol larger than it is in the open site.

^{a)} Present address: NASA AMES Research Center, Moffett Field, California 94035.

It is of interest to see if there are further large changes for this property as the cluster size is increased. In contrast to the binding energies, other properties like bond distance and vibrational force constants are quite similar for all sites between Be_{13}H and Be_{22}H .

COMPUTATIONAL MODEL

In the present work, a three-layer, 36 atom model of the (0001) surface of beryllium metal was used. Since the model has 14, 8, and 14 atoms on the three layers, it is referred to⁸⁻⁸ as Be_{36} (14, 8, 14). As in previous studies, the structure of the 36-atom cluster was that of the bulk beryllium metal. This approximation is consistent with the experimental finding that Be (0001) does not reconstruct.¹⁰ Calculations are performed for the isolated (bare) Be_{36} cluster and for Be_{36} clusters with an H atom added in one of four sites. These sites may be described by reference to Fig. 1, which is a schematic of the Be_{22} cluster or the top two layers of Be_{36} . For the directly overhead site, the H atom is placed directly above atom 11; for the open site, H is above the center of the triangle formed by surface atoms 12, 13, and 14; for the eclipsed site, H is above the triangle of atoms 11, 12, and 14; and for the bond midpoint site, H is above the midpoint of the line connecting atoms 12 and 14.

As in our earlier work, the self-consistent field (SCF) approximation was employed in conjunction with a minimum basis set of Slater functions, each expanded as a linear combination of three Gaussian functions. The basis sets used here are given in Ref. 8 (the Be basis is denoted there as minimum basis set IIb); for the reader's convenience, we give the details of the basis sets in the Appendix. Qualitatively, similar results are obtained with larger basis sets.⁸⁻¹² For

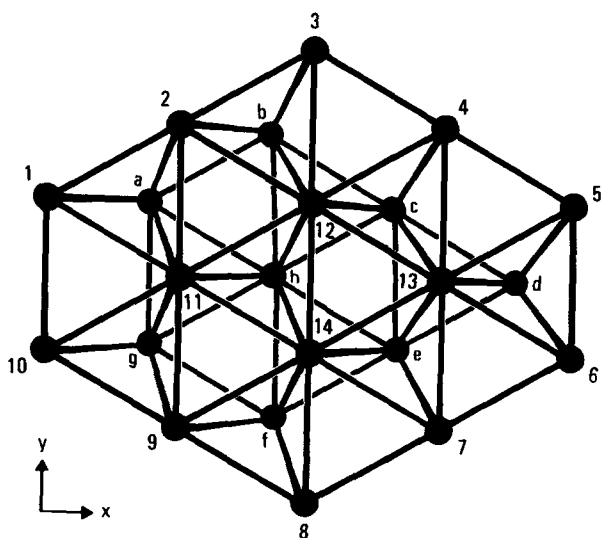


FIG. 1. The Be_{22} (14, 8) cluster studied in Ref. 8 and the top two layers of the Be_{36} cluster; the third layer is identical to the first. The top layer is numbered 1-14 and the second layer lettered a-h. The four sites studied are described in the Computational model section.

TABLE I. Orbital energies (in hartree) for the Be_{36} (14, 8, 14) cluster depicted in Fig. 1.

Core orbitals	Valence orbitals	Virtual orbitals
-4.6276	-0.7286	-0.0481
-4.6275	-0.6614	-0.0434
-4.6274	-0.6264	-0.0405
-4.6273	-0.6114	-0.0330
-4.6217	-0.5739	-0.0292
-4.6216	-0.5554	-0.0219
-4.6216	-0.5229	-0.0117
-4.6214	-0.5194	-0.0024
-4.6182	-0.4958	All others positive
-4.6138	-0.4823	
-4.6136	-0.4622	
-4.6136	-0.4397	
-4.6136	-0.4298	
-4.6117	-0.4082	
-4.6117	-0.3849	
-4.6063	-0.3845	
-4.6063	-0.3829	
-4.6061	-0.3654	
-4.6061	-0.3644	
-4.6017	-0.3523	
-4.6016	-0.3164	
-4.5922	-0.3083	
-4.5922	-0.2711	
-4.5921	-0.2706	
-4.5920	-0.2648	
-4.5914	-0.2585	
-4.5899	-0.2515	
-4.5898	-0.2446	
-4.5712	-0.2300	
-4.5711	-0.2172	
-4.5668	-0.2136	
-4.5668	-0.2099	
-4.5620	-0.2055	
-4.5620	-0.2011	
-4.5619	-0.1896	
-4.5618	-0.1825	

clusters up to Be_{10} (and Be_{10}H), the equilibrium bond lengths for the H were ~ 0.1 Å shorter with the large basis set than with the minimal basis sets; the H binding energies were ~ 10 kcal/mol greater with the larger basis.

ISOLATED Be_{36} CLUSTER

Orbital energies ϵ 's for the Be_{36} cluster are shown in Table I. The 1s-like orbitals, with ϵ values from -4.6276 to -4.5618 hartree, display a band width of 1.8 eV, the same as that obtained for the Be_{22} cluster. The occupied valence orbital energies range from -0.7286 to -0.1825 hartree, corresponding to a band width of 14.9 eV. For Be_{22} , the valence level width was somewhat less 13.2 eV. Also, as seen in Table I, the Be_{36} cluster yields eight virtual orbitals with negative orbital energies. For a conductor such as beryllium, the difference between the occupied and virtual orbital energies will become zero as the size of the finite cluster becomes sufficiently large. This follows because the I.P. and E.A. at the Fermi level of a conductor are the same: the ϵ 's represent Koopman's theorem approximations to these values and as the orbitals become sufficiently delocalized, relaxation

energies at E_f will go to zero. For Be_{36} , the gap between HOMO ($\epsilon = -0.183$ a.u.) and LUMO ($\epsilon = -0.048$ a.u.) is 3.7 eV; this is less than the 4.6 eV found for Be_{22} .

Also of interest for the isolated Be_{36} cluster is its cohesive energy. The total SCF energy for Be_{36} is -519.32907 hartree, while that of the Be atom is -14.38918 hartree. This means that the total binding energy is 827.4 kcal/mol or 23.0 kcal/mol per atom. The latter result is best evaluated by noting that the Be_{36} cluster contains 120 Be-Be near neighbor (first coordination shell) pairs or $3\frac{1}{3}$ near neighbor bonds per Be atom. In contrast, the bulk metal has precisely six bonds per atom. Only first coordination shell neighbors are considered to form bonds. Each bulk atom has 12 near neighbors, six in the plane, three above, and three below the plane. The 12 neighbors yield six bonds per atom after double counting is taken into consideration.

By such a geometric argument, one would expect no more than 56% of the bulk cohesive energy to be obtained from our Be_{36} model if the cohesive energy were determined by additive pair, two-body, interactions. This analysis should be combined with the fact that a minimum basis set SCF wave function yields about a third of the binding energy of tetrahedral Be_4 found from better wave functions which use larger basis sets and which include correlation.¹³ These considerations readily provide an explanation of why the present Be_{36} cohesive energy (23 kcal/mol) is much less than the 78 kcal/mol cohesive energy¹⁴ of the bulk metal.

The nature of the charge distribution in the cluster is examined by considering the Mulliken atomic populations. The atoms are labeled in Fig. 1. Those in the first layer are numbered 1-14; those in the second layer are labeled by the letters a-h. The populations of the third layer atoms, not shown in Fig. 1, are identical to the equivalent atoms in the first layer. (Recall that the Be_{36} cluster has C_{2v} symmetry.) The atomic populations, decomposed into s and p character, are given in Table II. The Be_{36} values are compared to those found for the two-layer Be_{22} (14, 8) cluster. The atomic populations for the first layer are very similar for both clusters. This suggests that they both provide

very similar descriptions of the electronic structure at a Be surface. However, the populations of the atoms in the middle layer are quite different between the Be_{36} and Be_{22} clusters. The atoms a and f have populations of 4.11 and 4.16 electrons in Be_{36} compared to 4.01 and 3.98 in Be_{22} . This difference would appear to represent a significant shift of charge away from the first and third layers to the middle layer. However, we should note that the middle layer of Be_{36} has twice the overlap population as the second (bottom) layer of Be_{22} ; thus, changes in the second layer of Be_{36} relative to the second layer of Be_{22} may be a computational artifact. On the other hand, the overlap populations between first and third-layer atoms of Be_{36} are likely to be very small; recall that the distance between these layers is $6.77a_0$. The fact that the differences between the first layer Be_{36} and Be_{22} populations are quite small is likely to be physically significant.

The most significant information from the population analysis concerns the hybridization of the valence electron character. The atomic $2s$ population (total s minus two $1s$ electrons) is inversely proportional to the number of near neighbors that the atom has; the $2p$ population increases with the number of neighbors. For atom h, which has the largest number 12 of near neighbors, the ratio of $2p$ to $2s$ character $1.50(p)/0.50(s) = 3.0$ is larger than for any other atom. The extent of s to p hybridization in SCF wave functions of alkaline earth compounds has been related to the strength of the bonds formed in these systems.¹³ If atom h is representative of an interior atom in Be metal, then a hybridization of sp^3 is appropriate for the bulk. The "internal" surface atoms (i.e., atoms 11, 12, 13, and 14 in Fig. 1) have nine near neighbors. They are likely to be representative of atoms on the Be (0001) surface, and they have hybridizations of roughly $sp^{2.3}$. The "edge" surface atoms (atoms 1, 10, 3, 8, 5, and 6) with the fewest near neighbors, only four in each case, have hybridization ratios between $sp^{1.13}$ and $sp^{1.23}$. The latter atoms, incidentally, are most like those occupying exposed positions (thought to be highly reactive) in stepped surfaces.² It might be argued cautiously that the reactivity of such exposed surface atoms is due to the fact that these atoms have less p character.

TABLE II. Mulliken atomic populations for the 36-atom beryllium cluster $\text{Be}_{36}(14, 8, 14)$. Values in parentheses are the comparable populations for $\text{Be}_{22}(14, 8)$. Atoms are numbered in Fig. 1.

Surface layer/(First=third)					Middle layer				
Atom	Number nearest neighbors	s	p	Total	Atom	Number nearest neighbors	s	p	Total
1 or 10	4	2.87(2.90)	1.07(1.08)	3.93(3.98)	a or g	9(6)	2.66(2.76)	1.45(1.25)	4.11(4.01)
2 or 9	6	2.78(2.70)	1.21(1.33)	3.99(4.04)	b or f	9(6)	2.59(2.75)	1.57(1.23)	4.16(3.98)
3 or 8	4	2.90(2.92)	1.04(1.02)	3.94(3.94)	c or e	10(7)	2.53(2.67)	1.53(1.35)	4.06(4.02)
4 or 7	5	2.76(2.80)	1.24(1.25)	4.00(4.05)	d	8(5)	2.72(2.93)	1.35(1.04)	4.07(3.97)
5 or 6	4	2.92(2.92)	1.04(1.05)	3.96(3.97)	h	12(9)	2.50(2.52)	1.50(1.47)	4.00(4.00)
11	9	2.58(2.59)	1.44(1.39)	4.02(3.98)					
12 or 14	9	2.59(2.61)	1.40(1.42)	3.99(4.03)					
13	9	2.64(2.63)	1.34(1.40)	3.98(4.03)					

^aNumber of neighbors for the second-layer atoms of Be_{22} is given in parenthesis.

TABLE III. Chemisorptive bond energies D_e in kcal/mol, equilibrium H-Be₃₆ distances r_e in Å, and vibrational frequencies ω_e in cm⁻¹. The distances reported are the normal (perpendicular) distances from the hydrogen atom to the (0001) surface. The notation Be_n(*i, j, k*) implies that the cluster includes *n* Be atoms, with *i, j*, and *k* of them being in the first, second, and third layers, respectively.

Cluster	Open site			Bond midpoint site			Eclipsed site		Directly overhead site		
	r_e	D_e	ω_e	r_e	D_e	ω_e	r_e	D_e	r_e	D_e	ω_e
Be ₁₃ (10,3)A	0.99	39.0	1187	1.05	44.8	1360	0.90	57.2
Be ₁₃ (10,3)B	0.94	58.3	1.41	31.1	2070
Be ₁₄ (14,0)	1.11	56.1	1150	1.17	53.1	1300	1.11	56.1	1.40	59.0	1960
Be ₂₂ (14,8)	0.94	55.1	1230	1.04	53.4	1360	0.97	51.9	1.39	31.4	2060
Be ₃₆ (14,8,14)	0.90	57.7	1200 ^a	1.00	43.7	1350	0.95	42.3	1.38	31.6	2020

^aAccurate to only two significant figures due to small energy difference resulting from too small a change in H position.

We note that even this rather large, 36 atom, cluster contains only a small number (4) of "internal" surface atoms (on layer 1 or 3); i.e., those likely to be representative of the atoms on an extended Be (0001) surface. Moreover, the cluster contains only one layer (layer 2) to represent bulk atoms. Thus, we do not expect the cluster to be able to give a particularly good description of the surface band structure or density of states. These properties are likely to depend strongly on the extended interactions among surface atoms and between surface and bulk atoms. However, we do expect that the cluster is able to provide a reliable description of the interaction between an adsorbate, in this case H, and the Be substrate. As we have discussed earlier,⁸ we expect that this interaction is dominated by, and depends strongly on, the localized aspects of the bond formed between the adsorbate and its near neighbors in the substrate.

CHEMISORPTION RESULTS

Table III summarizes the present structural and energetic results for the Be₃₆H system and compares these with previous results obtained from smaller clusters. The energetic ordering of Be₃₆ sites is the same as that found for Be₂₂, namely open > bond midpoint > eclipsed > directly overhead. There are two gross features of the chemisorption of H on the 36-atom cluster. The first is that the hydrogen atom has a slightly negative charge as with the smaller clusters. The second is that the open shell orbital is more delocalized for Be₃₆H than it was for the smaller clusters. Since the open shell orbital has virtually no H atom character, it should be, for a perfect surface, uniformly distributed over all the Be atoms. Thus, the localization of this orbital is a measure of edge effects in the cluster.⁸ We will discuss the results for the H atom binding energy (D_e), equilibrium bond distance (r_e), and vibrational frequency (ω_e) for each of the four adsorption sites individually.

This, and previous work,⁶⁻⁸ suggests that chemisorption at the directly overhead site is the least sensitive to cluster size. In fact, even the much smaller Be₁₀(7,3) model gives results very close to that found here for Be₃₆(14,8,14). However, as Table III illustrates, a single layer model such as Be₁₄(14,0), although providing a meaningful value of the H-surface equilibrium

distance and vibrational frequency, far overestimates the chemisorptive bond energy. This seems to be true, in general, for one layer clusters. For Be₇(7,0)-H, e.g.,⁸ the D_e = 71 kcal/mol is even larger than for Be(14,0)-H while the r_e = 1.43 Å and ω_e = 2100 cm⁻¹ are similar to the results for the larger clusters given in Table III. We have pointed out earlier,⁸ that the anomalous behavior of the D_e for the single layer clusters is related to the Be 2*p_z* role in the bonding. While the H-surface distance and vibrational frequency are reasonably well described by the small clusters, a moderate sized two- or three-layer cluster is needed as a good model for the bond energy associated with directly overhead chemisorption. This site is clearly the least stable of the four considered and has the longest surface-H distance.

For the Be₃₆ cluster, the open site is clearly the most favorable site for chemisorption. The open site was also energetically preferred for Be₂₂H, but by only 1.7 kcal over the bond midpoint site and 3.2 kcal over the eclipsed site. Like the directly overhead site, the open site changes only slightly with the addition of the third layer. The binding energy increases by only 2.6 to 57.7 kcal. The 1200 cm⁻¹ vibrational frequency predicted for Be₃₆ is close to the value obtained for Be₂₂H. The bond length is 0.04 Å shorter than for Be₂₂H. The change in bond length due to the addition of the second layer in going from Be₁₄(14,0) to Be₂₂(14,8) was 0.17 Å. This reduction in the bond length between the one-layer and the two- or three-layer clusters is also related to the role of the Be 2*p_z* character in the bonding.⁸ It is a result of a competition for the use of surface atom *p_z* functions for bonding between the layers of the cluster and for bonding between the cluster and the adsorbed H atom. When the H atom bonds to the one layer Be₁₄(14,0) cluster, the *p_z* character of the Be atoms is only used to form the BeH bond. However, when H bonds to the two-layer Be₂₂(14,8), the *p_z* character is also required to form bonds between the two layers of the cluster. As a result, the H atom equilibrium distance for Be₂₂ is closer to the surface. This allows the H to bond with Be *p_x* and *p_y* functions and permits the *p_z* character to be used for bonding between the surface layers. As expected, the additional layer makes a much smaller change in the *z* bonding, causing a much smaller change from Be₂₂ to Be₃₆.

TABLE IV. Gross atom Mulliken populations for the singly occupied open shell orbital for the Be_{22}H and Be_{36}H clusters. The atoms for the first, second, and third layers are listed separately; the numbering of the third-layer atoms is the same as that for the first layer (see Fig. 1). Populations, denoted n_e , are only given for atoms with more than 0.1e; the values for equivalent atoms are indicated within brackets.

Site	Top-layer		Second-layer		Third-layer	
	Atom	n_e	Atom	n_e	Atom	n_e
Open						
$\text{Be}_{22}\text{-H}$	1	0.42
	10					
$\text{Be}_{36}\text{-H}$	5	0.38	13	0.1
	6					
Bond midpoint						
$\text{Be}_{22}\text{-H}$	1	0.41
	10					
$\text{Be}_{36}\text{-H}$	5	0.14	13	0.1
	6					
Eclipsed						
$\text{Be}_{22}\text{-H}$	1	0.40
	10					
$\text{Be}_{36}\text{-H}$	5	0.3
					6	
Directly overhead						
$\text{Be}_{22}\text{-H}$	1	0.15	a	0.26
	10		g			
$\text{Be}_{36}\text{-H}$	c	0.10
			e			

Similar effects for r_e are also found for the bond midpoint site as noted below and in Table III.

The bond midpoint site exhibits the same 0.04 Å shortening of the bond and the same small change in vibrational frequency as both the open and overhead sites. However, unlike the other two sites, the binding energy becomes lower by 10 kcal/mol for $\text{Be}_{36}\text{-H}$ than for $\text{Be}_{22}\text{-H}$. Apparently, D_e is quite sensitive to the addition of third-layer atoms which are rather distant from the bonding berylliums 12 and 14. The bond length and vibrational frequency are more directly characteristic of the local bonding of H to the Be surface (cluster) and are not particularly sensitive to the addition of these distant neighbors.

Unlike the three other sites, we did not optimize the height of the hydrogen above the surface for the eclipsed site. This was not done because of the small changes for the three other sites and the broadness of the wells. We computed the eclipsed site at a bond length 0.02 Å shorter than the Be_{22} eclipsed site. As for the bond midpoint site, the binding energy for this site is sensitive to adding the distant, third-layer, atoms. It changes, becomes smaller, by 9.6 kcal/mol from the $\text{Be}_{22}\text{-H}$ value.

In our earlier work,⁸ we argued that the D_e would be

sensitive to the degree of localization of the open shell orbital of the $\text{Be}_n\text{-H}$ clusters. This localization arises because of edge effects in a finite cluster. Based on results for the bond midpoint site of Be_{22}H , we estimated that the open shell orbital localization would lead to a calculated value of D_e too large by ~6 kcal/mol. It seems worthwhile to examine whether there is a correlation between the localization of this orbital in the Be_{36} and Be_{22} atom clusters and the changes in the values for D_e . In Table IV, the localization of the open shell orbital is characterized for each site by giving the atomic populations on those atoms for which it is greater than 0.1 electrons. For the bond midpoint (BMP) and the directly over head (DOH) sites, there does seem to be such a correlation. For the DOH, the open shell orbital is not strongly localized for either $\text{Be}_{22}\text{-H}$ or $\text{Be}_{36}\text{-H}$ and the D_e 's for the two clusters are very similar. For the BMP, the orbital is localized on two atoms for $\text{Be}_{22}\text{-H}$ but it is rather delocalized for $\text{Be}_{36}\text{-H}$. The D_e changes by 10 kcal/mol between the two clusters. However, for the eclipsed (ECL) and open sites, the orbital is reasonably localized on two atoms for both the Be_{22} and Be_{36} clusters. For the ECL site, the change in D_e is much larger than for the open site. Thus, while the localization of the open shell orbital may be one reason for an uncertainty in the D_e , it is not the only reason. The presence of distant, second coordination shell neighbors also has a significant effect on D_e . In order to test whether still more distant neighbors could affect D_e , calculations on considerably larger clusters are necessary. While D_e for the DOH site appears to have converged, the $\text{Be}_{36}\text{-H}$ values of D_e for the other sites should be taken as uncertain by ~5 kcal/mol. It seems reasonable to believe that a highly accurate calculation of D_e is difficult within the molecular orbital cluster model. However, this should not be regarded as a particularly serious problem. The interaction between adsorbed atoms, not treated at all in our model calculations, may lead to changes in the D_e of the same order as the 5 kcal/mol uncertainty which we have estimated above. Moreover, it is conceivable that the presence of several neighboring chemisorbed H atoms could dampen the changes in D_e as a function of cluster size.

It would appear to be reasonable to regard the cluster D_e 's simply as guides to the relative site preference for chemisorption. Given our estimated uncertainty, the DOH site is the least stable and the open site is the most stable. The BMP and ECL sites are likely to have very similar binding energies intermediate between the DOH and the open sites. However, because of the uncertainty in the calculated D_e , we are not able to assign an order between them.

CONCLUDING REMARKS

The addition of a third layer of metal atoms to a finite cluster model has been shown to alter predicted chemisorptive bond energies by as much as 10 kcal/mol, or 20% in relative terms. However, such properties as the hydrogen distance above the surface and hydrogen vibrational frequency normal to the surface change by a much smaller amount ~4%. It is clear

TABLE AI. Contraction coefficients and exponents of the minimum basis sets for Be and H.

Type	Gaussian exponent	Contraction coefficient
Be		
s	30.249 896	0.154 329
	5.150 056	0.535 328
	1.491 243	0.444 635
s	2.581 50	-0.059 945
	0.156 762	0.596 039
	0.060 183	0.458 179
p	0.919 238	0.162 395
	0.235 919	0.566 171
	0.080 098	0.422 307
H		
s	2.946 080	0.154 329
	0.536 632	0.535 328
	0.145 234	0.444 635

that if all aspects of chemisorption are to be predicted to high accuracy, a very large cluster must be used, but that with a cluster conclusion, containing on the order of 22 atoms, the qualitative features of chemisorption can be determined.

ACKNOWLEDGMENTS

HFS was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy under contract No. W-7405-Eng-48. C.W.B. would like to acknowledge the hospitality of the IBM Research Laboratory.

APPENDIX: BASIS SETS

For Be, 1s, 2s, and 2p functions were used and, for H, a single 1s function was used. The Slater function exponents which were fit to three Gaussians are: Be(1s) $\zeta = 3.685$; Be(2s) $\zeta = 1.0$; Be(2p) $\zeta = 1.0$; and H(1s) $\zeta = 1.15$. The Gaussian exponents and contraction coefficients are given in Table AI.

¹E. W. Plummer and T. Gustafsson, *Science* **198**, 165 (1977).

²G. A. Somorjai, *Science* **201**, 489 (1978).

³*The Nature of the Surface Chemical Bond*, edited by T. N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979).

⁴E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.* **79**, 91 (1979).

⁵H. F. Schaefer, *The Electronic Structure of Atom and Molecules: A Survey of Rigorous Quantum Mechanical Results* (Addison-Wesley, Reading, Massachusetts, 1972).

⁶C. W. Bauschlicher, D. H. Liskow, C. F. Bender, and H. F. Schaefer, *J. Chem. Phys.* **62**, 4815 (1975).

⁷C. W. Bauschlicher, C. F. Bender, H. F. Schaefer, and P. S. Bagus, *Chem. Phys.* **15**, 227 (1976).

⁸C. W. Bauschlicher, P. S. Bagus, and H. F. Schaefer, *IBM J. Res. Dev.* **22**, 213 (1978).

⁹The interaction of molecular hydrogen (H₂) with Be (0001) has been studied experimentally, and dissociative chemisorption does not occur: J. J. Hurd and R. O. Adams, *J. Vac. Sci. Technol.* **5**, 183 (1968).

¹⁰See, for example, R. S. Zimmer and W. D. Robertson, *Surf. Sci.* **43**, 61 (1974); R. G. Musket, *ibid.* **44**, 629 (1974).

¹¹A. P. Humphries and H. D. Kaesz, *Prog. Inorg. Chem.* **25**, 145 (1979).

¹²C. W. Bauschlicher and P. S. Bagus, *Chem. Phys. Lett.* **90**, 355 (1982).

¹³C. W. Bauschlicher, P. S. Bagus, and B. N. Cox, *J. Chem. Phys.* **77**, 4032 (1982).

¹⁴D. R. Stull and H. Prophet, *JANAF Thermochemical Tables*, 2nd ed. NSRDS-NBS 37 (Superintendent of Documents, Washington, D.C., 1971).