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Publication Date
1975-12-01

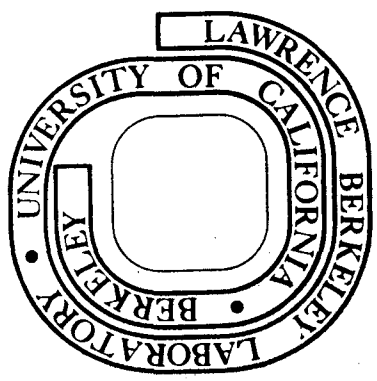# A REALISTIC CLUSTER MODEL FOR CHEMISORPTION

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December 1975

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A Realistic Cluster Model for Chemisorption[*]

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Abstract

A priori electronic structure theory has been used to model to (0001)
surface of beryllium metal. A cluster of 22 Be atoms was chosen for this
purpose, and four distinct sites for the chemisorption of atomic hydrogen
were investigated. Three of the sites yield chemisorptive bond distances
and energies of $\sim$ 1 Å and $\sim$ 50 kcal/mole, while for the fourth (the directly
overhead site) $\sim$ 1.4 Å and $\sim$ 30 kcal/mole are predicted.

The search for a distinctly molecular understanding of catalysis, surface chemistry, and surface physics has greatly accelerated over the past few years.[1] Until recently theory has played only a limited role[2] in the development of surface chemistry.[3] However during the past five years, quantitative molecular orbital theories have been used to provide considerable insight[4-25] into the properties of small metal clusters and the nature of the chemisorptive bond. Although most of these theoretical studies have employed semiempirical methods, ab initio techniques have been used in several cases.[7,9,10,17-19,23,25] Among the more important questions addressed theoretically have been (a) the convergence of metal cluster properties to the analogous properties of the infinite metal surface; (b) the nature of and number of surface atoms participating in the chemisorptive bond; and (c) the energetics and structures of various plausible sites (on the surface) for chemisorption.

In our previous work,[18,25] the chemisorption of atomic hydrogen on the (0001) surface[2] of Be metal was studied. The surface was modeled by metal clusters Be_n (n = 1-13) and four different sites for chemisorption considered. The choice of the Be_n-H system was discussed in detail in the earliest paper,[18] where we pointed out that the single-configuration Hartree-Fock approximation is particularly appropriate for this system. Although the H-(Be surface) system has not been investigated experimentally (the toxicity of beryllium is one obvious inhibiting factor), such studies are feasible[26] and should be forthcoming. LEED experiments[27] have already been reported for the (0001) surface of beryllium and show that the surface is not reconstructed--i.e., the surface atoms maintain the approximate positions given by the crystal structure of the metal. In addition the Auger electron

spectra of Be surfaces have been reported recently.[28] Thus we remain optimistic that the beryllium surfaces will in the near future serve as an important interface between experiment and rigorous theoretical methods.

Criticism of previous[4-25] cluster model studies of chemisorption centers about two points. First, the inherent reliability of some of the semi-empirical methods has been called into question. Secondly, and more germane to the present work, is the assumption that a surface can be realistically modeled by a small cluster of metal atoms. In this regard we note that the largest metal clusters studied to date involve only thirteen atoms.[21,25] The suspicion of cluster models seem strongest among physicists accustomed to using energy band methods. However, even among chemists there is disagreement concerning the size of the smallest realistic metal cluster model. For example, one well-thought-out response[29] to our previous Be_{10}-H studies[18] was that the ten atom cluster was about half as large as would be required for a truly realistic model.

The model adopted here for the (0001) surface[3] of beryllium consists of 22 atoms and is shown in the figure. This model allows a reasonable number of atoms in both the surface (14) and second (8) layers. The most serious deficiency of the Be_{22} model is the absence of any third layer atoms. Nevertheless, we feel that most chemists and physicists would agree that this model is sufficiently large that the results of carefully designed ab initio calculations should represent meaningful predictions concerning the nature of the chemisorptive bond.

The theoretical approach adopted here is essentially the same as that used in the study of the Be_{13} clusters.[25] That is, the structure of the

Be_{22} cluster is that of Be metal,[30] and a minimum basis set (1s, 2s, $2p_x$, $2p_y$, $2p_z$ on Be, 1s on H) was used within the single-configuration self-consistent-field (SCF) approximation. The latter approximation in terms of limited basis set size has been extensively tested[18,31] for systems as large as Be_{10}-H and found to be quite reasonable. Specifically, it appears that the type of minimum basis set adopted here yields SCF predictions within ∿ 5 kcal/mole for chemisorptive bond energies and within ∿ 0.1 Å for chemisorptive bond distances of the true Hartree-Fock limit[32] results. The four sites for chemisorption are[18] the open site (above the center of the triangle of atoms 5, 6, and 9), the eclipsed site (directly above the second-layer atom e), the bond midpoint site (above the bond connecting atoms 6 and 9), and the directly overhead site (above atom 6).

The present Be_{22}-H results are summarized and compared with results for the smaller clusters[18,25] in the Table. There it is apparent that the best convergence with respect to cluster size occurs for the directly overhead site. Specifically, the predicted chemisorptive bond energy is only 0.3 kcal/mole greater than that obtained with the Be_{13} model. In addition the predicted bond distance (in all cases the perpendicular distance from the H atom to the plane of the Be surface layer) is only 0.02 Å shorter than in Be_{13}-H. Perhaps most important, it is clear that chemisorption at the directly overhead site is qualitatively different from the three other sites.

As seen in the Tables, the open, eclipsed, and bond midpoint sites all have bond distances ∿ 1 Å and bond energies ∿ 50 kcal/mole. As described by Horiuti and Toya,[33] these three sites all correspond to "s states of chemisorbed hydrogen", for which the s adatom is interstitially located

between the electronic surface (perhaps defined in terms of <r> for the
isolated metal atom) and the metal surface. This classification is
especially useful since (a) such similar results are predicted for the three
s sites and (b) the other type of site ("r adatom", same as our directly
overhead site) described by Horiuti and Toya has very different characteristics.
However, while this _separation_ into r and s sites is quantitatively verified
here, our _ordering_ (s adatoms more strongly bound than r adatoms) with respect to
chemisorptive bond energy is quite the reverse of that predicted by these workers.[33]

An important observation is that some of the Be_{22}-H predictions are
significantly different from those of the largest systems previously studied.
Most strikingly, the energetic near-equivalence of the open, eclipsed, and
bond midpoint sites was not obvious from the Be_{13}-H predictions.[25] Interest-
ingly, however, we noted this near-equivalence in our original study[18] of
systems Be_n-H, n = 1-10. Thus it appears that there are significant
oscillations in predicted chemisorption characteristics as a function of
metal cluster size.

Finally we note that the Be_{22} cohesive energy of 22.0 kcal/mole is much
greater than that predicted for the smaller clusters. The largest cohesive
energy predicted previously was for Be_{13}, 14.2 kcal/mole. As noted earlier,[25]
there is a correlation between the realism of a particular cluster for
chemisorption studies and that cluster's predicted cohesive energy (the
larger the better) and ionization potential (low values being preferred).
The predicted ionization potential of Be_{22} is 4.60 eV, compared with
that for the two Be_{13} models, 4.70 and 4.32 eV. Thus for Be_n-H systems,
these two criterion for gauging the effectiveness of a cluster model are
given further credibility.

TABLE. Models of the chemisorption of atomic hydrogen by the (0001) surface of beryllium metal. The cluster notation $Be_{10}(7,3)$ implies a model with seven atoms for the surface layer and three atoms for the second layer. Bond distances r_e are in Å and chemisorptive bond energies D_e in kcal/mole.

Open Site			Eclipsed Site			Bond Midpoint Site			Directly Overhead Site		
Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e
$Be_3(3,0)$	1.25	19.1	$Be_4(3,1)$	1.24	28.7	$Be_4(4,0)$	1.26	70.1	$Be_1(1,0)$	1.42	46.4
$Be_5(4,1)$	1.02	23.2	$Be_5(4,1)$	1.15	30.1	$Be_5(5,1)$	1.14	32.4	$Be_7(7,0)$	1.43	71.3
$Be_6(6,0)$	1.18	47.3	$Be_7(6,1)$	1.11	40.8	$Be_{10}(10,0)$	1.17	45.3	$Be_{10}(7,3)$	1.43	27.3
$Be_6(3,3)$	1.11	55.3	$Be_{13}(10,3)$[a]	0.90	57.2	$Be_{13}(10,3)$	1.05	44.8	$Be_{13}(10,3)$	1.41	31.1
$Be_9(6,3)$	1.13	50.2		0.94	58.3	$Be_{22}(14,8)$	1.04	53.4	$Be_{22}(14,8)$	1.39	31.4
$Be_{13}(10,3)$	0.99	39.0	$Be_{22}(14,8)$	0.97	51.9						
$Be_{22}(14,8)$	0.94	55.1									

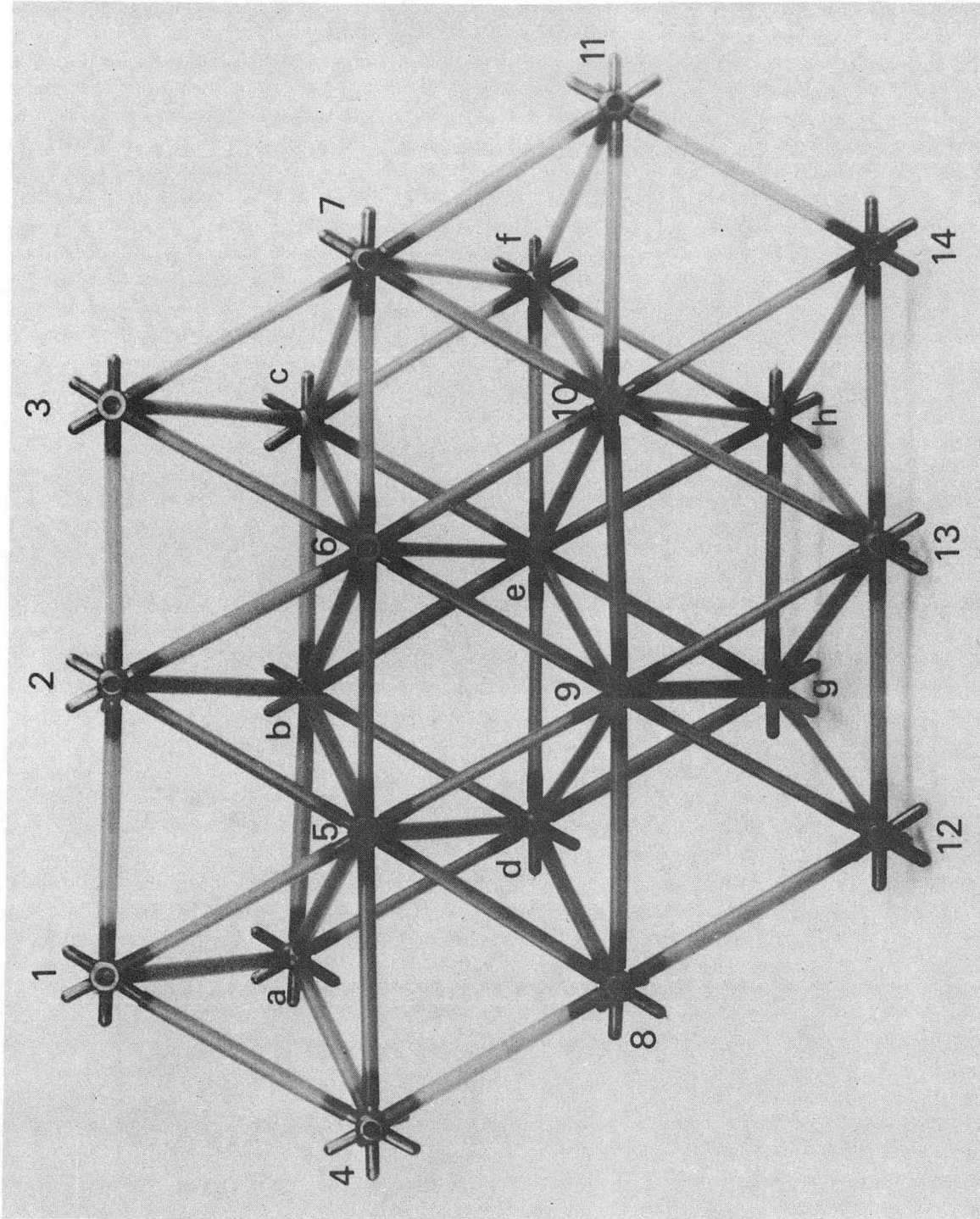[a] Note that in reference 25 that two distinct $Be_{13}(10,3)$ clusters were studied.

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Figure Caption. Model of the Be_{22} cluster used in the present theoretical study. The distance between adjacent atoms within a layer is 2.2866 Å, while that between adjacent atoms in different layers is 2.2255 Å. Surface atoms are labeled by the numbers 1-14, while second-layer atoms are labeled by the letters a-h.

Figure 1

XBB 7512-87737A