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# A Density Functional Study of the Interaction of Dihydrogen With $\text{Mo}_N$ Clusters ( $N = 2-8$ ). Adsorption and Dissociation of $\text{H}_2$ and Cluster Reconstruction After Desorption

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**ABSTRACT:** The interaction of small  $\text{Mo}_N$  clusters ( $N = 2-8$ ) with  $\text{H}_2$  is investigated using a GGA version of the density functional theory as implemented in the SIESTA code. Both the dissociation of  $\text{H}_2$  and the charge transfer to the metallic clusters are studied in detail to gain insight into the reactive properties of the aggregates in the gas phase. The reconstruction of the clusters after H elimination is also investigated to learn about the possibility of reutilization of the aggregates in future process. Present results indicate that  $\text{Mo}_7$  is particularly effective in dissociating  $\text{H}_2$ . © 2010 Wiley Periodicals, Inc. *Int J Quantum Chem* 111: 3201–3211, 2011

**Key words:** molybdenum clusters; hydrogen interaction; clusters reactivity; SIESTA; PBE

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## 1. Introduction

Small molybdenum clusters up to about 13 atoms have been thoroughly investigated in the last decades using several methodologies, most of those based on the density functional theory. In particular, a recent work of one of us focused on the geometric, electronic, and magnetic properties of  $\text{Mo}_{12}\text{Fe}$ ,  $\text{Mo}_{12}\text{Co}$ , and  $\text{Mo}_{12}\text{Ni}$  [1]. On the other hand, the studies concerning the interaction of those small aggregates with small reactive or probe molecules are scarce. It is possible to mention the work of Berces et al. [2] on small Nb and Mo clusters and their interaction with the probe  $\text{N}_2$  molecule using a GGA version of the density functional theory.

Molybdenum is a key component in hydrodesulfurization (HDS) catalysts, which are aimed at removing sulfur-containing compounds from crude oil during the refining process. HDS catalysts are usually formed by Co- and/or Ni-promoted  $\text{MoS}_2$  nanostructures supported on high-surface area species, typically  $\gamma$ -alumina [3, 4]. It is in general accepted that molybdenum atoms become reduced formally from  $\text{Mo}^{4+}$  to  $\text{Mo}^{3+}$  during the activation process of the HDS catalyst [5]. The activation of the catalyst is achieved in the presence of molecular hydrogen, which is responsible both for the reduction of molybdenum and for the elimination of surface sulfur atoms in the form of hydrogen sulfide. Those surface vacancies are then occupied by sulfur-containing compounds, such as thiophene or dibenzothiophene. It is then expected on the basis of the above mechanism that larger the amount of charge transferred from dihydrogen during dissociation, the more active the molybdenum aggregate will be in a potential HDS process.

On the other hand, it is a well-known fact that the identification of the reactive sites in heterogeneous catalysis can be aided by gas-phase studies of neutral and ionic clusters having an adequate size [6]. Thus, although the size of present  $\text{Mo}_N$  aggregates ( $N = 2-8$ ) is rather small and, moreover, they do not contain sulfur nor are supported, they could be thought of as the smallest possible models to study an HDS process from a purely gas-phase point of view.

As a continuation of our joint studies on the properties of small pure and bimetallic molybdenum clusters, as well as their reactivity features toward the modeling of catalytic processes, the interaction of  $\text{Mo}_N$  aggregates ( $N = 2-8$ ) with  $\text{H}_2$  is investigated within the framework of a GGA version of the density functional theory. Both the interaction

and dissociation of dihydrogen are studied in the first place, laying emphasis on the charge transferred from  $\text{H}_2$  to the metallic cluster, a necessary condition for the activation leading to the HDS process. The reconstruction of the aggregates after H elimination is examined in the second place.

Details of the computational method used in this article are given in Section 2. In Section 3, we present and discuss our results, and in Section 4, we summarize our main conclusions.

## 2. Computational Procedure

DFT pseudopotential calculations were performed with the code SIESTA (Spanish Initiative for Electronic Simulation of Thousand of Atoms) [7]. A linear combination of pseudoatomic orbitals is used as basis sets in that code. The atomic core is replaced by a nonlocal norm-conserving Troullier-Martins pseudopotential [8] that is factorized in the Kleinman-Bylander form [9] and may include nonlinear core correction terms to account for the significant overlap of the core charges with the valence  $d$  orbitals. The code allows to perform, besides the electronic structure calculation, geometry optimizations using a variety of algorithms.

In the present calculation, the exchange and correlation GGA density functional proposed by Perdew et al. [10], is used. The ionic Mo pseudopotential was generated using the atomic configurations  $4d^5 5s^1 5p^0$ , with 1.67, 2.30 and 2.46 a.u. cutoff radii, respectively. The core corrections were included using a radius of 1.2 a.u. That pseudopotential reproduced accurately the eigenvalues of different excited states of the isolated Mo atom. In the case of H, the configuration  $1s^1$  with a cutoff radius of 1.25 a.u. was used.

The valence space of molybdenum is described using a double- $\zeta$  doubly polarized (DZP) basis sets, i.e., basis that contains two orbitals having different radial form for both the  $4s$  and the  $4d$  shells and one orbital to represent the  $5p$  shell. Two orbitals have been also used to describe the  $1s$  shell of hydrogen. An electronic temperature of 25 meV and an energy cutoff of 200 Ry in the real space grid for numerical calculations involving the electron density were considered. Both larger energy cutoffs and lower electronic temperatures for some particular cases were also considered, but they did not substantially modify the results. All the calculations were performed in a cubic box of 20 Å, which is large enough for all the cluster sizes considered in this work.

Geometry optimizations were carried out with the help of the conjugate gradient algorithm [11]. Starting geometries were taken from pure Mo clusters [1] to study H<sub>2</sub> adsorption, whereas the aggregates that become distorted after adsorption were taken as starting points for reconstruction studies. Structural optimizations were stopped when the maximum force component at each atom in the system was smaller than 5 meV/Å.

Throughout this work, results are presented in terms of the atomization energy per atom, AE, which is defined as follows:

$$AE = \frac{E_{\text{Mo}_N} + E_{\text{H}_2} - E_{\text{Mo}_N\text{H}_2}}{N + 2} \quad (1)$$

where  $E_{\text{Mo}_N}$ ,  $E_{\text{H}_2}$  and  $E_{\text{Mo}_N\text{H}_2}$  are the equilibrium total electronic energies of the isolated cluster, dihydrogen, and the interacting system, respectively. Thus, a positive value of AE indicates that the interacting system is more stable than isolated cluster and molecule.

To evaluate whether the clusters become distorted or not after the interaction with H<sub>2</sub>, a very simple function of the geometries is introduced. Two matrices with all the Mo–Mo distances before and after the interaction are formed as follows:

$$D_{\text{initial}} = \begin{pmatrix} d_i(1,1) & d_i(1,2) & \dots & d_i(1,N) \\ d_i(2,1) & d_i(2,2) & \dots & d_i(2,N) \\ \vdots & \vdots & \ddots & \vdots \\ d_i(N,1) & d_i(N,2) & \dots & d_i(N,N) \end{pmatrix} \quad (2)$$

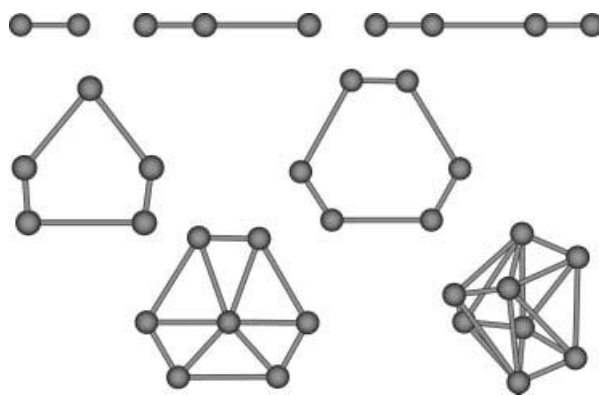
$$D_{\text{final}} = \begin{pmatrix} d_f(1,1) & d_f(1,2) & \dots & d_f(1,N) \\ d_f(2,1) & d_f(2,2) & \dots & d_f(2,N) \\ \vdots & \vdots & \ddots & \vdots \\ d_f(N,1) & d_f(N,2) & \dots & d_f(N,N) \end{pmatrix} \quad (3)$$

Then, the function  $D_{\text{dist}}$  is defined as follows:

$$D_{\text{dist}} = \frac{\sum_{i < j} |d_i(i,j) - d_f(i,j)|}{N(N-1)/2} \quad (4)$$

and could be thought of as a measure of the distortion underwent by the cluster normalized to the number of bonds.  $D_{\text{dist}}$  will be called distortion parameter from now on. Visual tests on the smaller clusters suggest that  $D_{\text{dist}}$  values greater than about 0.20 indicate an appreciable distortion from the starting geometry.

The energy barriers for the approach of the H<sub>2</sub> molecule to the aggregates are calculated for some selected cases. Only the Mo<sub>N</sub>–H<sub>2</sub> distance is allowed



**FIGURE 1.** Ground state geometries of Mo<sub>N</sub> clusters ( $N = 2-8$ ) taken from ref. [1].

to vary during the approach, whereas both the aggregate geometry and the H–H bond distance are kept frozen.

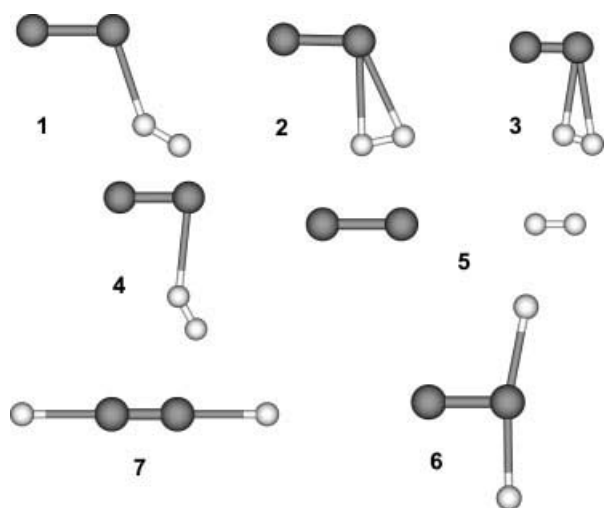
## 3. Results and Discussion

### 3.1. ADSORPTION AND DISSOCIATION OF H<sub>2</sub>

Figure 1 shows the ground state geometries for small molybdenum clusters up to eight atoms as obtained in [1], exception is only for  $N = 5$  where the house-like shape is more stable than the fan-like shape cluster previously reported. Several different sites involving a single molybdenum atom, a bond, or the center of triangular or square faces are considered for the interaction with dihydrogen, H<sub>2</sub>. As it is found that different sites for a given cluster size lead to the same geometry after adsorption and/or dissociation, only those sites providing different results are reported in tables.

At the present level of theory, the H<sub>2</sub> molecule shows an equilibrium distance of 0.79 Å and a dissociation energy of 4.21 eV. Those values are in good agreement with experimental data of 0.74 Å [12] and 4.52 eV [13], respectively.

Figure 2 shows the equilibrium geometries obtained for the Mo<sub>2</sub>–H<sub>2</sub> system. Table I lists the main features of those interactions. It can be seen that Mo<sub>2</sub> is able to dissociate dihydrogen in two different geometries only. In the first one, site 6 in Figure 2, the two hydrogen atoms lie on the same molybdenum atom. The atomization energy is 0.204 eV/at and the molybdenum dimer is not appreciably distorted. On the other hand, each hydrogen atom binds a different metal atom in site 7. The atomization energy is considerably larger in this site, 0.819 eV/at, and the Mo–Mo bond is slightly shortened with respect to



**FIGURE 2.** Equilibrium geometries for the interaction between  $\text{Mo}_2$  and  $\text{H}_2$  in different sites.

its equilibrium value. The electronic charge transferred to the metallic cluster amounts to  $0.328 |e|$  in site 7, whereas it is only  $0.090 |e|$  for site 6, suggesting a poor aggregate activation. The electron spin multiplicity of isolated molybdenum dimer does not change during dissociation.

The equilibrium geometries for the  $\text{Mo}_3\text{-H}_2$  system are depicted in Figure 3. Energetic and geometric features are shown in Table II.  $\text{Mo}_3$  is able to dissociate dihydrogen in several forms, see sites 1, 2, 4, 5, 11, and 12 in Figure 3. Only sites 2, 4, and 5 show an appreciable distortion parameter for the

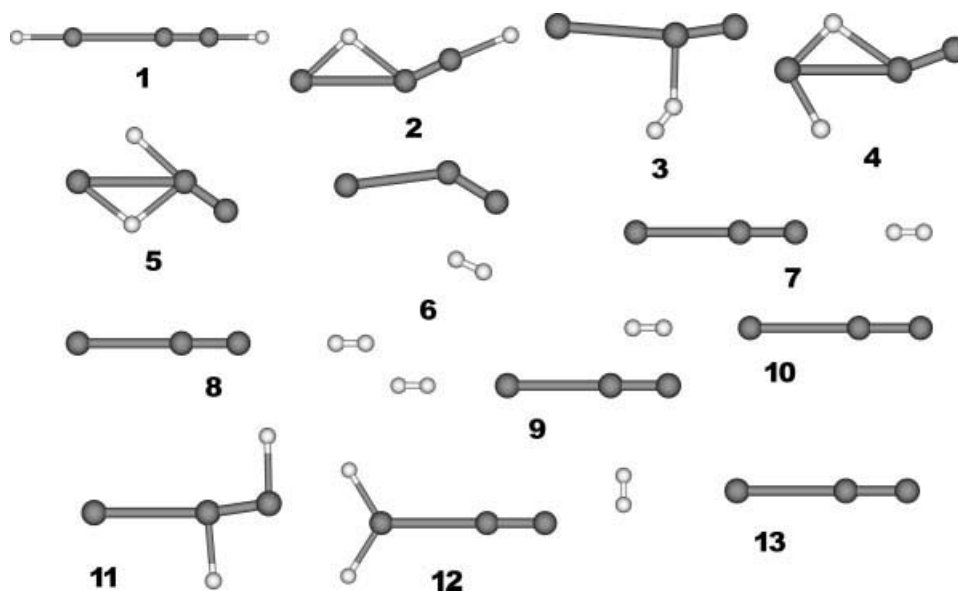
**TABLE I**  
Adsorption of dihydrogen on different sites of  $\text{Mo}_2$ .

Site	AE	$M_S$	$\Delta Q$	$D_{\text{dist}}$	Dissociates $\text{H}_2$ ?
1	0.204	1	0.009	0.017	No
2	0.033	3	— <sup>a</sup>	0.106	No
3	0.091	1	0.196	0.026	No
4	0.031	3	— <sup>a</sup>	0.224	No
5	0.135	1	— <sup>a</sup>	0.025	No
6	0.207	1	0.090	0.063	Yes
7	0.819	1	0.328	0.323	Yes

Atomization energies (AE, in eV/at), electron spin multiplicities ( $M_S$ ), charge transferred from dihydrogen to the site ( $\Delta Q$ , in  $|e|$  units) and distortion parameters ( $D_{\text{dist}}$ ) are shown. It is also indicated whether dihydrogen dissociates or not. See Figure 2 for label references.

<sup>a</sup> A small amount of charge transferred from the metallic aggregate to  $\text{H}_2$  is found for this site.

cluster. It can be seen that site 2 presents the highest atomization energy for the system and the largest distortion parameter. It is worth noting that sites 2, 4, and 5 exhibit the same bonding pattern after dissociation, that is, a hydrogen atom binds one molybdenum atom, whereas the other H atom binds two metal atoms. On the other hand, sites 11 and 12 present the lower atomization energies and different bonding patterns. Moreover, the distortion parameter indicates that the geometry of  $\text{Mo}_3$  remains almost unaltered after adsorption and dissociation. It is also interesting to note that no  $\text{H}_2$  dissociation is observed in site 6, even though the distortion



**FIGURE 3.** Equilibrium geometries for the interaction between  $\text{Mo}_3$  and  $\text{H}_2$  in different sites.

**TABLE II**  
Adsorption of dihydrogen on different sites of  $Mo_3$ .

Site	AE	$M_S$	$\Delta Q$	$D_{dist}$	Dissociates $H_2$ ?
1	0.212	7	0.366	0.113	Yes
2	0.415	5	0.653	0.259	Yes
3	0.125	7	0.077	0.091	No
4	0.289	5	0.770	0.188	Yes
5	0.250	7	0.681	0.233	Yes
6	0.113	7	0.052	0.181	No
7	0.046	5	— <sup>a</sup>	0.057	No
8	0.085	7	— <sup>a</sup>	0.034	No
9	−0.007	5	0.106	0.056	No
10	0.003	7	0.097	0.036	No
11	0.152	7	0.455	0.026	Yes
12	0.092	5	0.330	0.021	Yes
13	0.016	7	0.073	0.057	No

Atomization energies (AE, in eV/at), electron spin multiplicities ( $M_S$ ), charge transferred from dihydrogen to the site ( $\Delta Q$ , in  $|e|$  units) and distortion parameters ( $D_{dist}$ ) are shown. It is also indicated whether dihydrogen dissociates or not. See Figure 3 for label references.

<sup>a</sup> A small amount of charge transferred from the metallic aggregate to  $H_2$  is found for this site.

parameter is greater than 0.2. This fact indicates that a physical adsorption process could take place with a non-negligible distortion underwent by the metallic cluster. Interestingly, the largest charge transfers occurs in those sites in which  $H_2$  dissociation takes place. The amount of charge transferred from dihydrogen to the metallic aggregate ranges from

**TABLE III**  
Adsorption of dihydrogen on different sites of  $Mo_4$ .

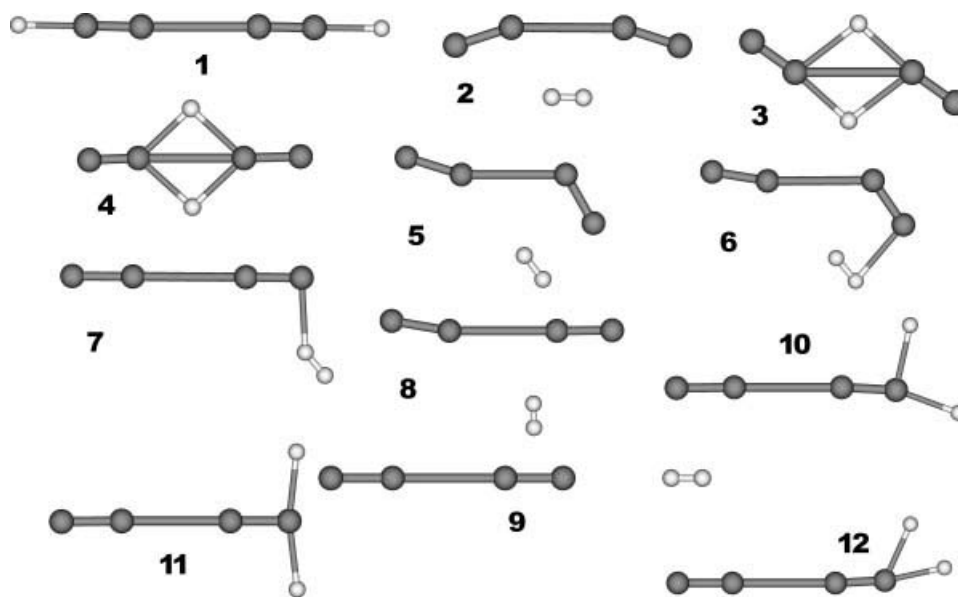
Site	AE	$M_S$	$\Delta Q$	$D_{dist}$	Dissociates $H_2$ ?
1	0.508	1	0.436	0.050	Yes
2	0.127	1	0.204	0.109	No
3	0.381	3	0.552	0.331	Yes
4	0.298	1	0.878	0.258	Yes
5	0.133	1	0.055	0.237	No
6	0.132	3	0.098	0.225	No
7	0.105	3	0.017	0.074	No
8	0.113	1	0.096	0.062	No
9	0.077	1	— <sup>a</sup>	0.020	No
10	0.083	3	0.256	0.059	Yes
11	0.118	1	0.188	0.037	Yes
12	0.049	3	0.358	0.084	Yes

Atomization energies (AE, in eV/at), electron spin multiplicities ( $M_S$ ), charge transferred from dihydrogen to the site ( $\Delta Q$ , in  $|e|$  units) and distortion parameters ( $D_{dist}$ ) are shown. It is also indicated whether dihydrogen dissociates or not. See Figure 4 for label references.

<sup>a</sup> A small amount of charge transferred from the metallic aggregate to  $H_2$  is found for this site.

0.330 to 0.770  $|e|$ , values which are larger than those found in case of the dimer. This fact could suggest a more effective activation process in  $Mo_3$  species. The electron spin multiplicity of the isolated trimer remains unaltered in some cases and decreases to a quintet state in some other sites.

Results for the  $Mo_4-H_2$  system are shown both in Table III and in Figure 4. Dihydrogen dissociation

**FIGURE 4.** Equilibrium geometries for the interaction between  $Mo_4$  and  $H_2$  in different sites.

**TABLE IV**  
**Adsorption of dihydrogen on different sites of Mo<sub>5</sub>.**

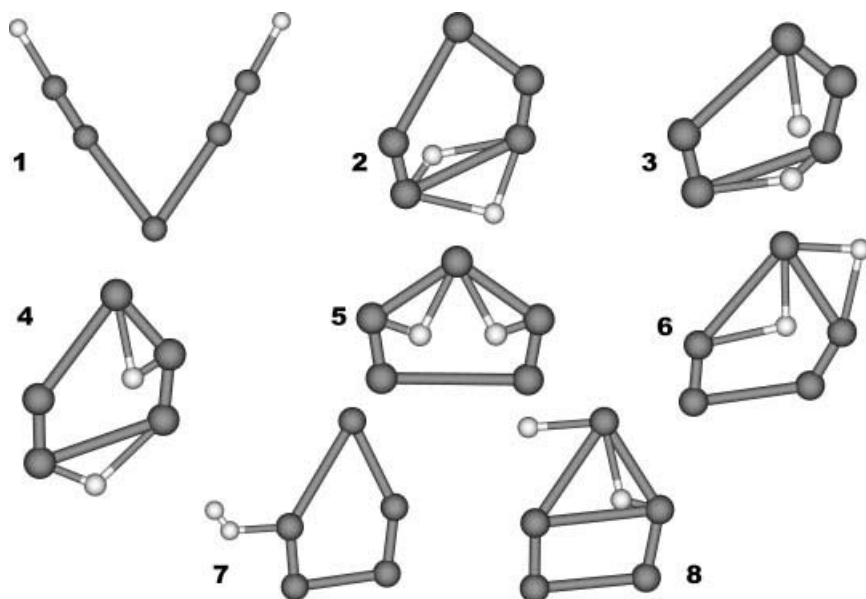
Site	AE	$M_S$	$\Delta Q$	$D_{\text{dist}}$	Dissociates H <sub>2</sub> ?
1	0.336	5	0.422	0.393	Yes
2	0.404	5	0.454	0.077	Yes
3	0.260	5	1.021	0.190	Yes
4	0.414	3	1.222	0.114	Yes
5	0.303	3	1.219	0.121	Yes
6	0.416	5	1.134	0.142	Yes
7	0.109	5	0.021	0.068	No
8	0.375	3	1.268	0.119	Yes

Atomization energies (AE, in eV/at), electron spin multiplicities ( $M_S$ ), charge transferred from dihydrogen to the site ( $\Delta Q$ , in  $|e|$  units) and distortion parameters ( $D_{\text{dist}}$ ) are shown. It is also indicated whether dihydrogen dissociates or not. See Figure 5 for label references.

by Mo<sub>4</sub> takes place in several sites. Interestingly, site 1 is able to dissociate H<sub>2</sub> with the highest atomization energy but without distorting the metal cluster. Hydrogen atoms bind terminal atoms in the linear Mo<sub>4</sub> cluster. Sites 3 and 4 dissociate dihydrogen, too, but in these cases, the molybdenum cluster is appreciably distorted, specially in site 3, in which even the linearity of the isolated cluster is lost. It is worth noting that in those cases, every hydrogen atom binds two molybdenum atoms, which are located in the middle of the linear aggregate. Sites 10, 11, and 12 are also able to break the H–H bond, but the atomization energy is considerably lower than the values

in the other sites. Moreover, the distortion parameter is very low in sites 10 to 12 and that could be related to the fact that the two hydrogen atoms bind the same metallic atom, a behavior already found in the dimer. The amount of charge transferred to the aggregates is only appreciable for sites 1, 3, and 4, the ones with the larger atomization energies. It can be seen in Table III that almost 0.9  $|e|$  are transferred from H<sub>2</sub> in site 4, which is considerably larger than the charge involved in sites 1 and 3. It is also worth to mention that the electron spin multiplicity of isolated Mo<sub>4</sub> is preserved in most cases.

Table IV and Figure 5 show the results obtained for the Mo<sub>5</sub>–H<sub>2</sub> system. It is interesting to see that the molybdenum pentamer is able to dissociate dihydrogen in all but one of the eight sites considered. Atomization energies are in a range from 0.260 to 0.416 eV/at. In line with the findings obtained for the tetramer, the sites with larger atomization energies, sites 6, 4, 2, and 8, exhibit an almost negligible distortion of the cluster after adsorption and dissociation. Interestingly, the dominant bonding pattern for those sites is the same, that is, every hydrogen atom binds two metallic atoms. That pattern is also observed in site 5, which presents a considerable atomization energy, too. Sites 3 and 8, on the other hand, shows a mixed bonding pattern, in which a H atom binds one Mo atom, whereas the second hydrogen atom binds two metallic centers. The largest distortion parameter is observed for site 1, in which the isolated pentamer is completely distorted



**FIGURE 5.** Equilibrium geometries for the interaction between Mo<sub>5</sub> and H<sub>2</sub> in different sites.

**TABLE V**  
**Adsorption of dihydrogen on different sites of  $\text{Mo}_6$ .**

Site	AE	$M_S$	$\Delta Q$	$D_{\text{dist}}$	Dissociates $\text{H}_2$ ?
1	0.103	1	0.034	0.119	No
2	0.448	1	0.576	0.523	Yes
3	0.347	1	0.578	0.123	Yes
4	0.330	1	0.586	0.136	No <sup>a</sup>

Atomization energies (AE, in eV/at), electron spin multiplicities ( $M_S$ ), charge transferred from dihydrogen to the site ( $\Delta Q$ , in  $|e|$  units) and distortion parameters ( $D_{\text{dist}}$ ) are shown. It is also indicated whether dihydrogen dissociates or not. See Figure 6 for label references.

<sup>a</sup> The H–H bond distance becomes enlarged by about 0.1 Å with respect to the equilibrium bond distance in this site. It is quite a small difference to be considered dissociated.

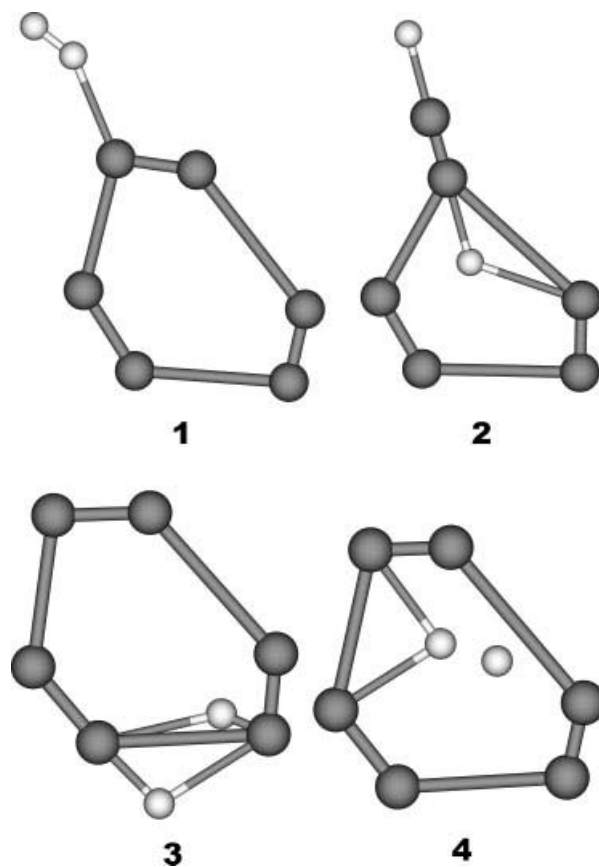
to adopt a v-shaped form. In this site each hydrogen atom binds one terminal molybdenum atom of the strongly distorted cluster. The larger charge transfers, however, are observed for sites 3 to 6 and 8. It is noteworthy that these are the first clusters for which more than 1.0  $|e|$  become transferred from dihydrogen. It can be seen in Table IV that the electron spin multiplicity of the isolated cluster is conserved in most cases, showing a decrease from a quintet state to a triplet one in three sites.

Only four sites produce relevant results for the  $\text{Mo}_6\text{--H}_2$  system as shown in Table V and Figure 6.  $\text{Mo}_6$  is able to break the H–H bond in two sites. Site 2 shows the largest atomization energy and an appreciable distortion and rearrangement with respect to the geometry of isolated cluster. Because of such rearrangement, a hydrogen atom binds a terminal molybdenum atom and the other H atom binds two Mo atoms. Interestingly, the other site, in which dihydrogen dissociates exhibits a small distortion parameter indicating that the cluster geometry remains almost unchanged after both the adsorption and dissociation take place. In this site, both hydrogen atoms bind the same two molybdenum atoms in a double bi-coordinated form. The charge transferred in sites 2 and 3 is less than 0.6  $|e|$ , an amount that can be considered rather small to lead to an important activation in the case of the hexamer. The electron spin multiplicity is preserved in all sites.

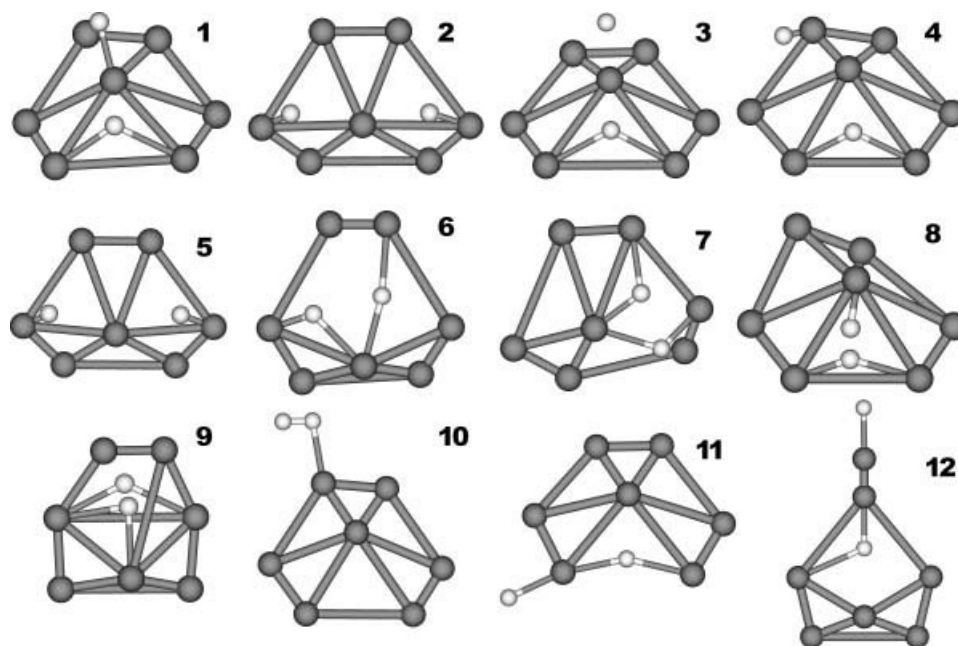
$\text{Mo}_7$  is found to be specially efficient to dissociate dihydrogen, as can be seen from Figure 7 and Table VI. The molybdenum heptamer is able to dissociate  $\text{H}_2$  in 11 different sites, most of them with atomization energies in the range from 0.177 to 0.308 eV/at. The metallic cluster undergoes a modest distortion in most sites. The more impressive distortion

is found in site 12, in which various Mo–Mo bonds become broken. The dominant bonding pattern for this cluster size seems to be characterized by a H atom binding one Mo atom, whereas the second hydrogen atom becomes bound to two metallic centers. That pattern is observed in six sites. Two sites exhibit a bonding pattern in which every hydrogen atom binds one molybdenum atom. In the other three sites, every H atom binds two molybdenum atoms. In line with the efficiency to dissociate  $\text{H}_2$ , the charge transferred to the clusters is larger than about 1.2  $|e|$  for all sites except for site 9. Moreover, sites 2, 4, and 5 exhibit a charge transfer of almost 2.0  $|e|$  indicating that dihydrogen converts into two protons after dissociation. Those sites seem to be good models for HDS. The electron spin multiplicity of the isolated cluster is preserved in the majority of the sites.

Figure 8 and Table VII summarizes the results for the  $\text{Mo}_8\text{--H}_2$  system. The octamer breaks the H–H bond in four sites. Interestingly, the four sites



**FIGURE 6.** Equilibrium geometries for the interaction between  $\text{Mo}_6$  and  $\text{H}_2$  in different sites.



**FIGURE 7.** Equilibrium geometries for the interaction between  $\text{Mo}_7$  and  $\text{H}_2$  in different sites.

show important atomization energies and distortion parameters that indicate strong deformations after adsorption and dissociation. The site with the larger atomization energy, site 7, also exhibits the larger distortion parameter. It can also be seen in Figure 8 that the metallic cluster undergoes an important distortion after adsorption and dissociation in site 4. The dominant bonding pattern is clearly the one in which every H atom binds two molybdenum atoms. The charge transfer for those sites that dissociate  $\text{H}_2$  lies in a wide range from 0.442 to 1.266  $|e|$ , the larger values found for sites 1 and 7. The electron spin multiplicity of the isolated cluster is preserved in all sites.

To get a deeper insight into the dissociation of  $\text{H}_2$  by small molybdenum clusters, the energy barriers for the approach of  $\text{H}_2$  to selected sites are studied at the same level of theory used throughout the investigation. Only those sites with atomization energies and electronic charge transfers larger than 0.250 eV/at and 1.000  $|e|$ , respectively, are considered. Results are shown in Table VIII. The energy barriers are calculated with respect to isolated  $\text{H}_2$  and  $\text{Mo}_N$ . It is seen in the table that sites 3 and 6 of molybdenum pentamer show no energy barrier for the approach of dihydrogen. This fact could be understood in terms of the relatively small enlargement underwent by the H–H bond distance after dissociation in those sites with respect to the other

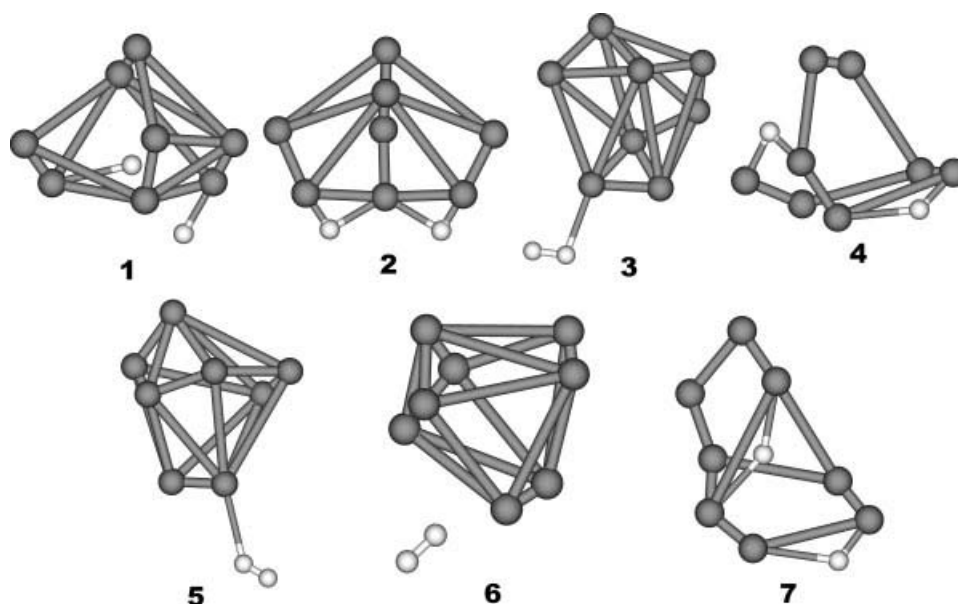
$\text{Mo}_5$  sites. Sites 4 and 5 of the molybdenum pentamer exhibit rather large energy barriers, above 0.76 eV. On the other hand, site 8 of  $\text{Mo}_5$ , all sites of molybdenum octamer and most sites of  $\text{Mo}_7$  present much lower energy barriers, ranging from 0.12 to 0.26 eV. Those values represent exponential factors of about

**TABLE VI**  
Adsorption of dihydrogen on different sites of  $\text{Mo}_7$ .

Site	AE	$M_S$	$\Delta Q$	$D_{\text{dist}}$	Dissociates $\text{H}_2$ ?
1	0.301	1	1.496	0.091	Yes
2	0.296	1	1.910	0.245	Yes
3	0.275	3	1.572	0.126	Yes
4	0.278	1	1.988	0.178	Yes
5	0.308	3	1.994	0.223	Yes
6	0.256	3	1.746	0.301	Yes
7	0.205	3	1.515	0.241	Yes
8	0.177	3	1.430	0.128	Yes
9	0.205	3	0.084	0.242	Yes
10	0.067	3	0.132	0.085	No
11	0.233	3	1.564	0.229	Yes
12	0.265	3	1.192	0.534	Yes

Atomization energies (AE, in eV/at), electron spin multiplicities ( $M_S$ ), charge transferred from dihydrogen to the site ( $\Delta Q$ , in  $|e|$  units) and distortion parameters ( $D_{\text{dist}}$ ) are shown. It is also indicated whether dihydrogen dissociates or not. See figure 7 for label references.





**FIGURE 8.** Equilibrium geometries for the interaction between Mo<sub>8</sub> and H<sub>2</sub> in different sites.

$1 \times 10^{-2}$  to  $5 \times 10^{-5}$  in the Arrhenius equation at 300 K. This suggests that modest pre-exponential factors should provide velocity constants well above the unity.

### 3.2. RECONSTRUCTION AFTER DESORPTION

One of the key concepts in catalysis, both homogeneous and heterogeneous, is the possibility of reconstruction of the catalyst after a given process takes

place. Thus, to shed some light into the reconstruction of small molybdenum clusters after molecular H<sub>2</sub> or H atoms elimination, geometries corresponding only to those cases with the larger atomization energies for every cluster size were allowed to relax to a new minimum, except for the rather trivial case of Mo<sub>2</sub>.

**TABLE VII**  
Adsorption of dihydrogen on different sites of Mo<sub>8</sub>.

Site	AE	M <sub>S</sub>	ΔQ	D <sub>dist</sub>	Dissociates H <sub>2</sub> ?
1	0.325	1	1.266	0.237	Yes
2	0.285	1	0.442	0.227	Yes
3	0.082	1	0.090	0.032	No
4	0.350	1	0.764	0.273	Yes
5	0.075	1	— <sup>a</sup>	0.048	No
6	0.076	1	— <sup>a</sup>	0.036	No
7	0.435	1	1.000	0.618	Yes

Atomization energies (AE, in eV/at), electron spin multiplicities (M<sub>S</sub>), charge transferred from dihydrogen to the site (ΔQ, in |e| units) and distortion parameters (D<sub>dist</sub>) are shown. It is also indicated whether dihydrogen dissociates or not. See Figure 8 for label references.

<sup>a</sup> A small amount of charge transferred from the metallic aggregate to H<sub>2</sub> is found for this site.

**TABLE VIII**  
Energy barriers (EB, in eV) for the approach of H<sub>2</sub> to some selected sites.

Cluster-site	EB	TB
Mo <sub>5</sub> -site 3	— <sup>a</sup>	
Mo <sub>5</sub> -site 4	1.04	3.71
Mo <sub>5</sub> -site 5	0.76	3.74
Mo <sub>5</sub> -site 6	— <sup>a</sup>	
Mo <sub>5</sub> -site 8	0.14	4.20
Mo <sub>7</sub> -site 1	0.25	3.83
Mo <sub>7</sub> -site 2	0.12	2.65
Mo <sub>7</sub> -site 3	0.26	2.82
Mo <sub>7</sub> -site 4	0.17	3.99
Mo <sub>7</sub> -site 5	0.23	4.00
Mo <sub>7</sub> -site 6	0.21	3.86
Mo <sub>7</sub> -site 12	0.31	3.98
Mo <sub>8</sub> -site 1	0.20	3.89
Mo <sub>8</sub> -site 7	0.18	4.04

The top of the barriers (TB, in Å) are also reported.

<sup>a</sup> No energy barrier is found for this site.

Both site 2 of  $\text{Mo}_3\text{-H}_2$  and site 1 of  $\text{Mo}_4\text{-H}_2$ , see Figures 3 and 4, relax to their original, linear structures after eliminating the H atoms.

Site 6 of  $\text{Mo}_5\text{-H}_2$ , see figure 5, relax to a structure that is about 0.04 eV/at above the ground state of  $\text{Mo}_5$ , which is shown in Figure 1. A quintet electronic state is obtained, however, for the reconstructed geometry in agreement with the spin multiplicity of the ground state.

The important distortion underwent by  $\text{Mo}_6$  when dihydrogen is dissociated forming site 2, see figure 6, prevents the aggregate from relaxing to the geometry of the isolated cluster. The relaxed geometry corresponds to a local minimum located about 0.17 eV/at above the ground state of  $\text{Mo}_6$ . Nevertheless, the electron spin multiplicity of the reconstructed geometry is a singlet, as it is in the ground state.

As expected, the modest distortion underwent by  $\text{Mo}_7$  when  $\text{H}_2$  becomes dissociated in site 5, see figure 7, allows the aggregate to relax to the ground state of the heptamer.

Site 7 in the  $\text{Mo}_8\text{-H}_2$  system, see Figure 8, presents an appreciable distortion parameter that prevents  $\text{Mo}_8$  from relaxing to the ground state. That local minimum is, however, very close in energy to the ground state and presents the same electron spin multiplicity.

#### 4. Conclusions

The interaction of small  $\text{Mo}_N$  clusters ( $N = 2\text{--}8$ ) with  $\text{H}_2$  was studied within the framework of a GGA version of the density functional theory as implement in the SIESTA code, with emphasis in the dissociation of molecular hydrogen and the reconstruction of molybdenum aggregates after remotion of hydrogen atoms.

Molybdenum clusters are able to dissociate dihydrogen for every considered size.  $\text{Mo}_5$  and  $\text{Mo}_7$  clusters are particularly efficient to break the H-H bond, as dissociation is observed in all but one of the sites considered for those sizes in this work.

$\text{Mo}_2$  shows the largest interaction energy with  $\text{H}_2$  amounting to more than 0.8 eV/at. Interaction energies exhibited by  $\text{Mo}_3$  to  $\text{Mo}_8$  clusters are considerably lower, being their larger values within a range from about 0.3 eV/at to about 0.5 eV/at.

The greater distortions underwent by the clusters after  $\text{H}_2$  dissociation are observed in  $\text{Mo}_6$ ,  $\text{Mo}_7$ ,

and  $\text{Mo}_8$ . The other cluster sizes also present appreciable distortions, but to a minor extent than those mentioned for the larger aggregates.

For all cluster sizes,  $\text{H}_2$  transfers some electronic charge to molybdenum aggregates. The amount of charge transferred ranges from 0.3  $|e|$  for  $\text{Mo}_2$  to 2.0  $|e|$  for  $\text{Mo}_7$ .

The calculation of the energy barrier for some selected sites showed that sites 3 and 6 of  $\text{Mo}_5$  exhibit no barrier for the approach of  $\text{H}_2$ . On the other hand, site 8 of  $\text{Mo}_5$ , sites 2 to 6 of  $\text{Mo}_7$ , and sites 1 and 7 of  $\text{Mo}_8$  present barriers sufficiently small to suggest that those sites could present velocity constants above the unity if pre-exponential factors are sufficiently large.

Finally, the reconstruction of molybdenum clusters after H atoms elimination was studied to mimic the possibility of reutilization of the aggregates in a gas-phase catalytic process. Only  $\text{Mo}_3$ ,  $\text{Mo}_4$ , and  $\text{Mo}_7$  were able to relax to their original structures and electronic spin multiplicities.

Taking into account that molybdenum aggregates should be able not only to dissociate dihydrogen with the lowest possible energy barrier and to undergo a reductive process, but to reconstruct after hydrogen desorption, too, to be considered as good gas-phase models for catalysis reactions, the above results indicate that sites 2 to 6 of  $\text{Mo}_7$  could be taken as serious candidates for such models.

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