Binding of Hydrogen Molecules by a Transition-Metal Ion

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Using self-consistent-field molecular-orbital theory, we show that the interaction of hydrogen molecules with a Ni^+ ion is characteristically different from that with a neutral Ni atom. While hydrogen chemisorbs dissociatively on the neutral metal atom, it is bound to the cation in its molecular form. The atomic bonding is a consequence of the Pauli exclusion principle whereas the bonding of the molecular hydrogen results from an electrostatic interaction. We predict that a Ni^+ ion can bind at least six hydrogen molecules.

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The interaction of hydrogen with metals and metal surfaces has been studied for many years. It is commonly understood that a H_2 molecule breaks up into individual atoms at about 0.5 Å from the metal surface and atomic chemisorption ensues [1]. No evidence exists, to our knowledge, of molecular chemisorption of hydrogen on the metal surface or inside the bulk metal. However, pairing of hydrogen mediated by a metal atom in rare-earth systems [2] and molecular hydrogen in Si [3] have recently been observed.

Little is known about the interaction of hydrogen with small metal particles consisting of a few atoms. The first evidence that hydrogen interaction with metal clusters may be fundamentally different from bulk came from recent experiments [4] on hydrogen reactivity and absorption. The reactivity was found to change by orders of magnitude by changing only a few atoms in the cluster. Equally interesting was the observation [5] that metal clusters might be able to absorb as many as eight hydrogen atoms per metal atom even though no corresponding bulk metal hydride exists. Not much is known regarding why clusters behave so differently towards hydrogen than bulk or whether hydrogen is bonded to the cluster in atomic or in molecular form.

In this Letter we show that hydrogen interacts the same way with a neutral atom as it does with the atoms on surfaces and in the bulk. However, the interaction of hydrogen with a metal ion is fundamentally different. In the case of the neutral atom, an electron is transferred from the metal atom to the approaching H_2 molecule and, in keeping with the Pauli exclusion principle, occupies the antibonding orbital of the molecule. This, in turn, breaks the molecular bond in favor of atomic bonding between the dissociated hydrogen atoms and the metal atom. However, when a H_2 molecule approaches a transition-metal ion, it becomes energetically inefficient for the metal atom to donate an electron to H_2 since the second ionization potential of the metal atom is rather high. Instead, the ion polarizes the H_2 molecule and the bonding between the ion and the H_2 molecule is governed by a dipole mechanism. We predict that a single Ni^+ ion can trap up to ten hydrogen molecules.

Our results are based on first-principles calculations of the total energies and equilibrium geometries of $Ni(H_2)_n$ and $Ni^+(H_2)_n$ clusters. We have used the self-consistent-field linear combination of atomic orbitals molecular-orbital theory through GAUSSIAN 88 softwave [6]. An unrestricted Hartree-Fock (UHF) method was used to calculate the electrostatic and exchange contributions to the potential. The correlation was included using the effect of the valence electrons and the Möller-Plesset many-body perturbation theory up to the fourth order (MP4SDQ). The geometries were optimized using the numerical gradient technique at all levels of calculation. The procedure is well described in the literature [6,7] and the reader is referred to these publications for details. It is sufficient to mention here that we have used the d^9s^1 configuration for the Ni atom with a split-valence Huzinaga basis [8] modified to include polarization. The final contraction scheme for this basis is $(13s,10p,5d/4s,3p,2d)$. For hydrogen, we have used the 6-311G** basis [6] with a contraction scheme of $(5s,1p/3s,1p)$.

To gain confidence on the accuracy of our predictions, a critical analysis of the choice of the basis and the convergence of the perturbation series in the correlation contribution to energy is necessary. It is well known that the d^8s^2 and d^9s^1 configurations of Ni give rise to states quite close in energy. In bulk Ni, the configuration is d^8s^2 while in the atom it is d^9s^1. We have tested both these configurations and have found that Ni_2 is stable only if the d^9s^1 configuration is used. This is in agreement with results of others [9]. Using the above basis we have calculated the binding energies and bond lengths of Ni_2, NiH, and Ni^+He. The results are compared with experimental values [10,11] in Table I. It is evident that the agreement is good. In the literature, however, other authors [9] have used more extensive wave functions for Ni involving numerous extra functions as well as up to f orbitals. It has been found [12] that these additions have only a minor effect and in view of the complexity of our calculations on Ni^+H_{2n} clusters we have decided not to employ the extra functions and the f orbitals. We have also studied the effect of including triple excitations on the binding energy of Ni^+H_2 clusters. We find that the use of MP4SDTQ and MP4SDQ gives rise to binding energies of 0.53 and 0.50 eV, respectively. This difference

TABLE I. Comparison between the calculated and experimental binding energies and bond lengths of Ni_2, NiH, and Ni^+He.

Diatomic	Bond length (Å)		Binding energy (eV)	
cluster	Theory	Expt.	Theory	Expt.
Ni_2	2.49	2.30	2.17	2.39
NiH	1.57	1.48–1.64	2.97	3.07
Ni^+He	1.97		0.11	0.14

is not very significant and therefore, MP4SDQ was used for the remaining calculations.

We next address the question of convergence in the perturbative treatment of correlation corrections. For Ni^+H_2 the change in the *total energy* from the UHF value by including a correlation at the second order (MP2) is −0.146 hartree. Subsequent inclusion of third-order (fourth-order) correlation changes the MP2 (MP3) energy by +0.028 (−0.018) hartree units. Similar results are found for Ni^+H_4, Ni^+H_8, and Ni^+H_{12}. Note that the fourth-order correction is an order of magnitude smaller than the MP2 correction.

We now discuss the results of the neutral Ni atom interacting with H_2 molecules. The optimized geometry of the NiH_2 is linear as depicted in Fig. 1(a) where the H_2 molecule has dissociated and the hydrogen atoms are bonded on either side of the Ni atom. Every effort to search for a molecular chemisorption state has failed in this case. The Mulliken charge analysis reveals that the Ni atom "donates" 0.23 electron to each of the hydrogen atoms. This electron is forced to occupy the antibonding orbital of the H_2 molecule due to the Pauli exclusion principle. The antibonding electron weakens the molecular bond and the hydrogen molecule dissociates. The binding energy ΔE of the NiH_2 cluster calculated against dissociation to H_2 and Ni, namely,

$$\Delta E = E(\mathrm{Ni}) + E(\mathrm{H_2}) - E(\mathrm{NiH_2}), \qquad (1)$$

is 1.36 eV. The definition in Eq. (1) is designed to yield a positive binding energy in situations where binding is energetically favorable. To see if additional hydrogen atoms can decorate the Ni atom we attempted a global geometry optimization of NiH_3 and NiH_4 by following the gradient technique. In each of these studies two hydrogen atoms tried to form a molecule and move away from the cluster during the optimization procedure. We, therefore, studied the NiH_4 cluster where the hydrogen molecules were not allowed to form. Three geometries were tried: (i) H atoms at the corners of a square with the Ni at the center, (ii) a square pyramid with the H atoms at the corners of the base and the Ni at the apex, and (iii) a tetrahedral unit of H atoms with Ni at the center. The Ni-H bond distance was optimized. The last configuration was energetically the lowest of the three. Still this was found to be 3.19 eV higher than the dissociation product of one Ni atom and two hydrogen molecules. Thus we conclude that a neutral Ni atom cannot, on its own, bind more than two H atoms.

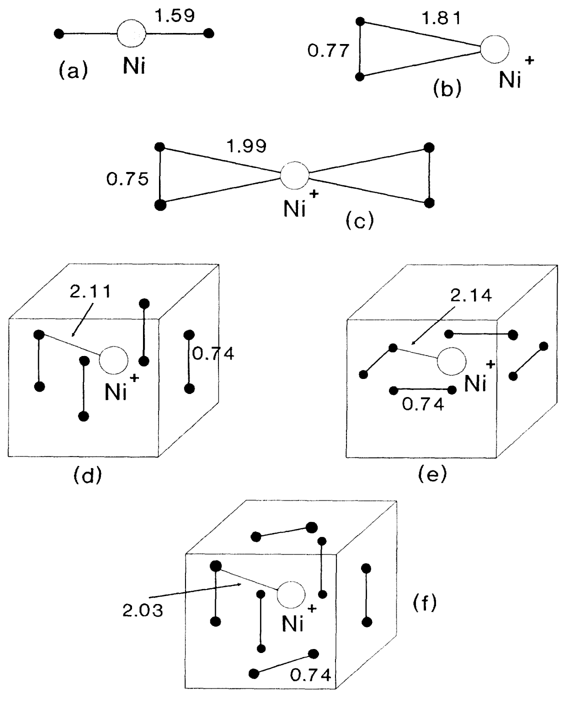

FIG. 1. Geometries of studied neutral and cationic nickel-hydrogen clusters.

The situation for a Ni^+ ion interacting with H_2 molecules is, however, entirely different. In Fig. 1 we give the equilibrium geometries of $Ni^+(H_2)_n$ clusters [13]. The corresponding binding energies per H_2 molecule,

$$\Delta E^+ = \{E(\mathrm{Ni}^+) + nE(\mathrm{H_2}) - E[\mathrm{Ni}^+(\mathrm{H_2})_n]\}/n, \qquad (2)$$

are given in Table II. Many interesting observations can be made from Fig. 1 and Table II. (i) Note that the bond length between the two hydrogen atoms is 0.77 Å in Ni^+H_2 and it quickly approaches the molecular bond length of 0.74 Å in the $Ni^+(H_2)_4$ cluster. In order to ensure that hydrogen does not bind to Ni^+ in atomic form, we have calculated the total energies of the Ni^+H_4 cluster by confining the hydrogen atoms to lie at the vertices

TABLE II. Binding energies and Mulliken populations of a $Ni^+(H_2)_n$ cluster.

Cluster	Binding energy per H_2 molecule ΔE^+ (eV)	Mulliken population	
		Ni^+	H
Ni^+H_2	0.50	27.17	0.91
$Ni^+(H_2)_2$	0.46	27.27	0.93
$Ni^+(H_2)_4$ [Fig. 1(d)]	0.36	27.40	0.95
$Ni^+(H_2)_4$ [Fig. 1(e)]	0.32	27.40	0.95
$Ni^+(H_2)_6$	0.26	27.60	0.95

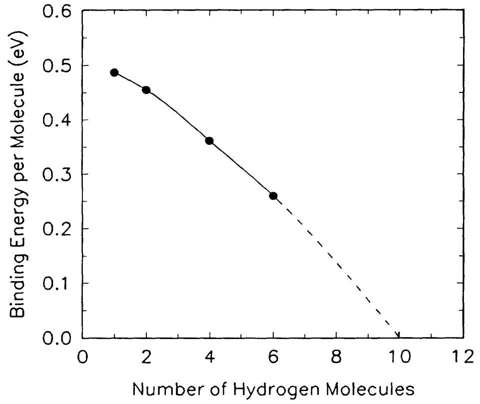

FIG. 2. Variation of binding energy per H_2 molecule (ΔE^+) with the number of H_2 molecules in the $Ni^+(H_2)_n$ clusters.

of either a square or a tetrahedron with Ni^+ occupying the central location. The relevant bond distances were optimized. The planar and three-dimensional structures are respectively 6.85 and 7.22 eV above the molecular dissociation defined in Eq. (2). We have also calculated the total energies of Ni^+H_8 by confining hydrogen atoms at the corners of a cube and the Ni^+ ion at its center. This structure with optimized bond length is 8.47 eV above the molecular dissociation limit. Thus hydrogen is chemisorbed on the Ni^+ ion in its molecular form [14]. This has never been seen for hydrogen interacting with a metal surface. (ii) The charge on the hydrogen atom is less than unity and approaches an asymptotic value of 0.95. Thus hydrogen "donates" a small amount of electrons to the Ni^+ ion. This is different from hydrogen in bulk metals or on metal surfaces where it always "accepts" electrons from the metal atom. This contrasting behavior is caused by the fact that it is more difficult to extract electrons from a positive ion than the neutral atom since the second ionization potential is much larger than the first. Instead, a Ni^+ ion polarizes the surrounding molecule and the binding takes place by simple electrostatic interaction [15]. (iii) The ΔE^+ decreases as the number of H_2 molecules increases. This is due to the fact that with each additional H_2 molecule the Ni^+ ion gets closer to the neutral state which in turn reduces the electrostatic binding. The extrapolation of results in Fig. 2 would indicate that no more than ten H_2 molecules can be bound to one Ni^+ ion. This number, however, is likely to increase if a more extensive basis set is used [15].

In order to understand to what extent the purely electrostatic interaction can explain the molecular chemisorption on the Ni^+ ion, we consider the $Ni^+(H_2)_4$ cluster in Fig. 1(d). Assuming that the charges are localized on the individual atoms and using the Mulliken populations from Table II and interatomic distances from Fig. 1(d), the electrostatic potential energy per H_2 molecule can be calculated easily from Coulomb's law. This yields a binding energy of 0.36 eV which is identical to the fully self-consistent value in Table II. Such an analysis for smaller clusters (e.g., Ni^+H_2) gives an overbinding compared to the results in Table II. This indicates that the problem of a Ni^+ ion surrounded by many H_2 molecules is analogous to the problem of electron solvation in water and ammonia clusters.

To our knowledge, experimental results on the trapping of H_2 molecules by the Ni^+ ion are not available at present. However, Ni^+He has been found [11] to be stable and has a binding energy of 0.14 eV. Since both He and H_2 have closed shells, we expect $Ni^+(H_2)_n$ to be similar to $Ni^+(He)_n$ in terms of stability. To confirm this, we have calculated the binding energy of Ni^+He using the procedure mentioned above to be 0.11 eV. Experiments on larger clusters of He and H_2 interacting with Ni^+ are strongly encouraged.

This study also opens some other interesting possibilities. For example, how does the trapping of H_2 molecules depend on the chemistry of the metal ion? Systematic studies of transition- and noble-metal ions interacting with H_2 clusters would be most illuminating. These are currently under investigation.

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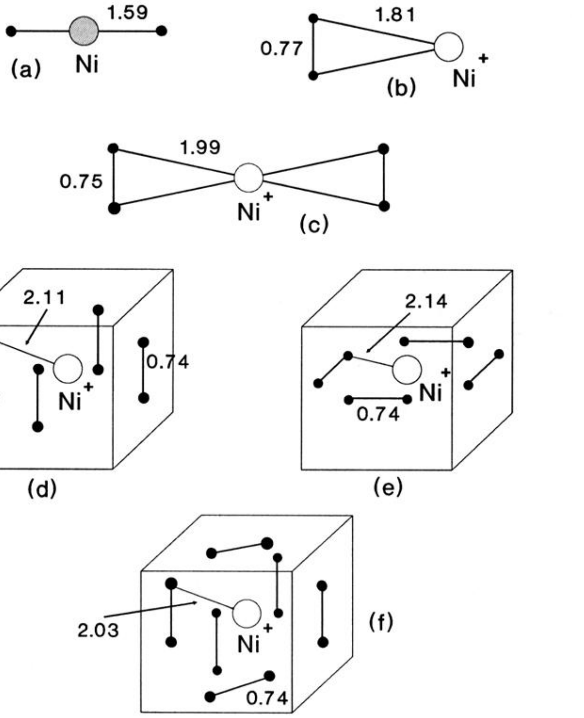
[13] The determination of equilibrium geometries by requiring the forces to vanish at every atomic site may sometimes lead to transition states. To distinguish between the transition states and the ground state, we have calculated the vibrational frequencies for Ni^+H_2 and $Ni^+(H_2)_2$ systems at the MP2 level for the geometries given in Figs. 1(b) and 1(c). The frequencies were all real and positive, signifying that these geometries correspond to the ground states. For the Ni^+H_2 system, the optimized bond lengths Ni^+-H and H-H from the MP2 calculations were 1.78 and 0.76 Å, respectively. As observed from Fig. 1, these are very close to the MP4 results. The corresponding bond lengths for the $Ni^+(H_2)_2$ system are 1.87 and 0.87 Å, respectively. For larger $Ni^+(H_2)_2$ clusters we confined the atoms in the geometries given in Fig. 1 and optimized the respective bond lengths at the MP4 level. The resulting clusters are *bound* with respect to dissociation into H_2 molecules and Ni^+ ion. Any other configuration with lower total energy would only result in stronger binding.

[14] A recent calculation based on the local-density approximation by S. N. Khanna and F. Reuse on $Ni^+(H_2)_4$ cluster has confirmed molecular bonding of hydrogen.

[15] Since polarization is the dominant mechanism for the binding of the H_2 molecules, we have analyzed the effect of H basis sets on the binding energy. We have repeated the calculation on the Ni^+H_2 system using the (*7s3p2d/5s3p2d*) basis. This yields a binding energy of 1.0 eV which is significantly higher than the value in Table II. It is, however, very difficult to perform the calculations for larger clusters with this extensive basis. What is important is that the hydrogen is bound in the molecular form and a better basis will clearly enhance the binding, thus pushing the number of H_2 molecules that can be attached to a Ni^+ ion much higher. The physics of the problem, however, will remain unchanged.



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