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Interaction of H_2 and He with metal atoms, clusters, and ions

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The binding energy, equilibrium geometry, and electronic structure of molecular hydrogen and helium atoms interacting with Ni, Cu, Co, and Al atoms and cations have been calculated using self-consistent-field linear combination of the atomic-orbitals–molecular-orbital method. The exchange interaction between the electrons is treated using the unrestricted Hartree-Fock theory. Correlation is included using Möller-Plesset perturbation theory up to the fourth order. The accuracy of the calculation is tested by comparing the results of the ground-state spin and binding energy with available experiments on dimers. While a neutral metal atom is found to dissociate the H_2 molecule, the metal cations bind the H_2 molecule associatively and with rather large binding energy. The binding of the He atom to a metal cation is found to be analogous to that of a H_2 molecule since both possess closed electronic shells. The number of hydrogen molecules and He atoms that can be bound to a metal cation at a given temperature and gas density is studied using the effective-medium approximation and density-functional theory. The results are compared with recent experiments.

I. INTRODUCTION

The interaction of hydrogen with metals has been studied extensively for more than a century, and much is known about the natures of its dissociation, binding site, and heats of formation.[1] While hydrogen may not form a stable hydride phase in most metals, it is known to chemisorb on all metal surfaces. This usually proceeds via a two-step process: molecular physisorption followed by a barrier and atomic chemisorption on surface sites. The height of the barrier depends on the electronic structure of the metal. If the metal is characterized by predominantly *s* electrons, the barrier is high. If the metal, on the other hand, has primarily *d* electrons, the barrier to dissociation can be very small. There are no situations known to the authors where hydrogen is molecularly chemisorbed on a metal surface, although associative physisorption of H_2 on metal surfaces is likely.[2]

Recently there has been much interest in studying the interaction of hydrogen with metal clusters.[3] Unlike bulk metals, metal clusters are characterized by a large surface-to-volume ratio. In addition, the electron levels in a metal cluster are discrete, while in a metal they merge to form bands. It has been shown[4] that the discrete level structure causes the screening and energetics of the hydrogen to be very different inside a small cluster than in the bulk. These unique features of clusters cause one to wonder if the nature of interaction of hydrogen with metal clusters may not be fundamentally different from that in bulk metals. In this context, the charge state of a cluster may also become very important. For example, the interaction of hydrogen with bulk metal may not be dependent on whether the metal is charged or neutral. On the other hand, in a metal cluster where the number of valence electrons are few, the charge state of a cluster, whether negative or positive, may significantly affect its interaction. This expectation makes the study of hydrogen interaction with neutral and charged clusters very interesting.

That the large surface-to-volume ratio of metal clusters contributes to unique properties can be seen from an early experiment by Parks *et al.* on Fe clusters[5] interacting with hydrogen. They observed that the number of adsorbed hydrogen atoms equals the number of Fe atoms in the Fe cluster. As the cluster becomes larger the ratio of hydrogen to Fe atom decreases, as it should since Fe does not form a stable metal-hydride phase. This can be understood qualitatively simply by considering the surface area of the cluster onto which hydrogen atoms can be attached. Assuming the Fe clusters to be spheres, it is easy to show that the number of hydrogen atoms, *m*, chemisorbed on an *n* atom cluster varies as $n^{2/3}$. This provides an excellent description of the data for $n > 20$, but deviates strongly for smaller clusters. This kind of treatment[6,7] also fails to adequately describe the melting of small clusters. Here one has to consider the cluster geometry as well as its electronic structure in detail.

Since the properties of metal clusters and their reaction with hydrogen are particularly sensitive to size in the case of small clusters, we have recently studied the interaction of hydrogen with small Li clusters[8] using quantum chemistry methods.[9] Other authors have studied the interaction of hydrogen with small Pd and Ni clusters using density-functional theory.[10] In each case the H_2 molecules were found to chemisorb dissociatively on neutral clusters as they do on metal surfaces. However, cluster-specific properties of hydrogen can be obtained if one studies other properties such as the ionization potentials of hydrogenated metal clusters. These undergo an abrupt

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change when the number of hydrogen-induced levels equals the number of valence electrons in the metal cluster. The maximum number of hydrogen atoms that can be bound per metal atom of the cluster was found to depend upon the number of "free" electrons in the cluster.

In the present work we have systematically studied the binding energy and geometries of H_2 molecules and He atoms interacting with neutral atoms and positive ions of Al, Cu, Co, and Ni. These systems have different electronic structures. While Al^+ and Cu^+ have closed electronic shells, Ni^+ and Co^+ have open shells. By studying the interaction of these ions with H_2 we see if the chemistry of the ion is important in binding hydrogen. We have also studied the interaction of Ni^+ with He. This study is of interest because He possesses a closed electronic shell like H_2, but its polarizability is about a factor of 4 smaller than that of H_2. A recent experiment has also reported on the binding energy of the Ni^+He dimer.[11] We have investigated the effect of the temperature and density of the H_2 and He gas on the number of molecules and atoms that can be bound to a metal cation using the Atkins model.[12,13] The results are compared with a recent experiment by Kemper and Bowers.[14] Finally we comment on the binding of H_2 molecules to cluster ions.

In Sec. II we briefly describe our theoretical procedure, and we present the results in Sec. III. A summary of our conclusions is given in Sec. IV.

II. THEORY

The total energy of the cluster was calculated self-consistently using the molecular-orbital theory. The cluster wave function was constructed from a linear combination of atomic orbitals, namely

$$\Psi_i(\mathbf{r})=\sum_{\nu} C_{i\nu}\phi_\nu(\mathbf{r}-\mathbf{R}_\nu) , \tag{1}$$

where ϕ_ν's are the atomic orbitals centered on the νth site and $C_{i\nu}$'s are the coefficients of linear combination. The atomic orbitals were fitted to a set of Gaussian functions. The basis sets used for various atoms are given in Table I by the usual notations used in quantum chemistry. For Ni we have tested both the d^8s^2 and d^9s^1 configurations. It was found that the Ni_2 dimer is stable[15] only if one uses the d^9s^1 configuration, which is the configuration in the atom. $C_{i\nu}$'s were obtained by solving the Hartree-Fock equation[9] self-consistently. In this procedure, the exchange interaction in the Hamiltonian was treated using the unrestricted Hartree-Fock approximation. The correlation contribution was then calculated using the Möller-Plesset perturbation theory up to fourth order (MP4).[9] We have also studied the effect of including single, double, triple, and quadrupole excitations (MP4SDTQ) as well as single, double, and quadrupole excitations (MP4SDQ).

TABLE I. Basis sets for atoms used in the calculation.

Atom	Basis set
H[a]	$(7s,3p,2d/5s,3p,2d)$
He[a]	$(5s,1p,1d/3s,1p,1d)$
Al[a]	$(16s,10p/4s,3p)$
Co[b]	$(13s,10p,5d/4s,3p,2d)$
Ni[b]	$(13s,10p,5d/4s,3p,2d)$
Cu[a]	$(13s,7p,4d/4s,2p,1d)$

[a] See details in Ref. 28.

[b] See details in Ref. 27.

The geometry of the cluster was optimized[16] by minimizing the total energy. The force at every atom site was calculated using the gradient technique, and the atoms were moved along the path of steepest descent until the forces vanished. To ensure that the cluster has reached the global minimum, several initial atomic configurations were tried, and total energies were compared among the various local minima.

The binding energies of clusters involving hydrogen and He atoms are defined by the relations

$$\Delta E_{\mathrm{H}}=E[M]+nE[\mathrm{H}_2]-E[M(\mathrm{H}_2)_n] , \tag{2}$$

$$\Delta E_{\mathrm{He}}=E[M]+nE[\mathrm{He}]-E[M(\mathrm{He})_n] , \tag{3}$$

where $E(M)$, $E(\mathrm{H}_2)$, and $E(\mathrm{He})$ are the total energies of the metal atom/cation, hydrogen molecule, and He atom, respectively. $E[M(\mathrm{H}_2)_n]$ and $E[M(\mathrm{He})_n]$ are total energies of the optimized clusters containing the metal atom/cation and n H_2 molecules or n He atoms, respectively. The electronic structure of the clusters was studied by analyzing the Mulliken charge population and the charge-density distribution.

III. RESULTS AND DISCUSSIONS

A. Testing the basis set and level of correlation

In a quantum chemical description, it is possible to obtain quantitatively accurate results if one is not restricted to the use of a limited basis and/or limited level of correlation. However, as one increases either the level of the atomic basis or the level of the correlation correction or both, the computational time increases so rapidly that it becomes impossible to calculate the total energy of even a dimer. Choices, therefore, have to be made if one is interested in calculating the equilibrium geometries and binding energies of a large number of clusters consisting of a few atoms each. It is, however, important to assess the reliability of the predicted results by first comparing the theoretical results with experiment in known systems. This is done in Table II, where we compare the binding energy, bond length, and ground-state spin multiplicity of a number of dimers. We note that in most cases the bond lengths are predicted to an accuracy of better than 0.1 Å, and the binding energy to an accuracy of 0.2 eV. The only exception is in the case of Ni_2, where the bond length differs from experiment[17] by 0.2 Å. Calculations[18] in the literature are available for Ni_2, where the basis sets have included up to f orbitals. In view of the increase in computer time and the large number of clusters to be

TABLE II. Comparison between calculated and experimental results.

Diatomic cluster	Ground state Theory	Ground state Expt.[b]	Bond length, Å Theory	Bond length, Å Expt.	Binding energy[a], eV Theory	Binding energy[a], eV Expt.
Al_2	${}^3\Sigma^-$	${}^3\Sigma^-$	2.52	2.466	1.32	1.55
Ni_2	${}^1\Sigma_g^+$	c	2.49	2.30	2.17	2.36
AlH	${}^1\Sigma^+$	${}^1\Sigma^+$	1.66	1.648	3.27	3.06
CoH	${}^3\Phi$	${}^3\Phi$	1.50	1.542	2.99	2.923
CuH	${}^1\Sigma^+$	${}^1\Sigma^+$	1.35	1.463	3.98	2.73
NiH	${}^2\Delta$	${}^2\Delta$	1.57	1.48–1.64	2.97	≤3.07
Al^+H	${}^2\Sigma^+$	c	1.60	1.602	0.80	
Co^+H	${}^4\Phi$	${}^4\Phi^d$	1.48		2.12	1.98±0.06[d]
Cu^+H	${}^2\Sigma^+$	${}^2\Sigma^{+d}$	1.38		1.03	0.92±0.13[d]
Ni^+H	${}^3\Delta$	${}^3\Delta^d$	1.52		1.51	1.68±0.08[d]

[a] Defined in theory part.

[b] Reference 17, unless otherwise noted.

[c] Not available.

[d] Reference 3.

considered, we decided to sacrifice the marginal improvement in accuracy and used the basis functions given in Table I.

In Table III we give a detailed comparison of the total energies calculated using various levels of correlation. The accuracy in the convergence procedure was carried to the sixth decimal place. We note that it is certainly necessary to go beyond the Hartree-Fock approximation, and it is sufficient to include correlation only at the MP4SDQ level. In what follows we discuss the energetics and electronic structure of equilibrium clusters at the MP4SDQ level of theory.

TABLE III. Comparison of energies for different perturbation levels of correlation.

Type of cluster	Total Energies (a.u.)	Differences[a] (a.u.)
H_2	RHF = −1.1330	
	EUMP2 = −1.1639	0.0309
	EUMP3 = −1.1697	0.0058
	UMP4(SDQ) = −1.1712	0.0015
	UMP4(SDT) = −1.1712	0.0000
Al^+	UHF = −241.6520	
	EUMP2 = −241.6778	0.0258
	EUMP3 = −241.6862	0.0084
	UMP4(SDQ) = −241.6892	0.0030
	UMP4(SDTQ) = −241.6892	0.0000
Al	UHF = −241.8564	
	EUMP2 = −241.8853	0.0290
	EMP3 = −241.8950	0.0097
	UMP4(SDQ) = −241.8983	0.0033
	UMP4(SDTQ) = −241.8985	0.0003
Al^+H_2	RHF = −242.7865	
	EUMP2 = −242.8446	0.0581
	EUMP3 = −242.8590	0.0144
	UMP4(SDQ) = −242.8634	0.0044
	MP4(SDTQ) = −242.8640	0.0007
AlH_2	UHF = −243.0159	
	EUMP2 = −243.0827	0.0668
	EUMP3 = −243.0971	0.0144
	UMP4(SDQ) = −243.1006	0.0035
	UMP4(SDTQ) = −243.1013	0.0008
Binding Energies[b]	Al^+H_2: SDQ = 0.081 eV	
	SDTQ = 0.099 eV	0.018 eV
	AlH_2: SDQ = 0.846 eV	
	SDTQ = 0.859 eV	0.010 eV

[a] Difference between two adjacent levels, e.g., for AlH_2, UHF-EUMP2 = 0.066 779 03 a.u.

[b] Binding energies are not necessary at equilibrium position.

B. Binding of the H_2 molecules

We first discuss the binding of a single H_2 molecule with a metal atom/cation. In Figs. 1–4, we plot the energetics [Eq. (2)] and the H-H separation as functions of distance between the metal atom/cation and center of mass of the H_2 molecule for all the systems we studied.

A general feature in all these figures is that the potential-energy curves exhibit two minima separated by an energy barrier corresponding to associative and dissociative binding. In the case of H_2 interacting with a neutral metal atom, the deeper minimum corresponds to the dissociative state. For the cation it corresponds to the associative state. The distance between hydrogen atoms in all cases remains close to the molecular value until they reach the barrier, at which point the dissociation of the molecule into atoms is abrupt and the H-H distance rises sharply. This situation is to be compared with Fig. 5, where we give the geometries of $M\mathrm{H}_2$ and $M^+\mathrm{H}_2$ clusters (M=Al, Ni, Co, Cu). Note that for $M\mathrm{H}_2$, the metal atom has inserted itself into the H-H bond, while in $M^+\mathrm{H}_2$ the H-H bond has remained molecular.

The difference between the nature of hydrogen bonding with a neutral metal atom and cation arises due to different electronic processes operative in the H_2 interactions. In the case of neutral metal atoms, electrons are transferred from the metal atom to the antibonding state of the H_2 molecule. This destabilizes the H-H bond and leads to the dissociation of the H_2 molecule. The hydrogen atoms then can gain energy by binding to the metal atoms in atomic form. The charge transfer to hydrogen causes the H atom to exist in a slightly anionic form, as

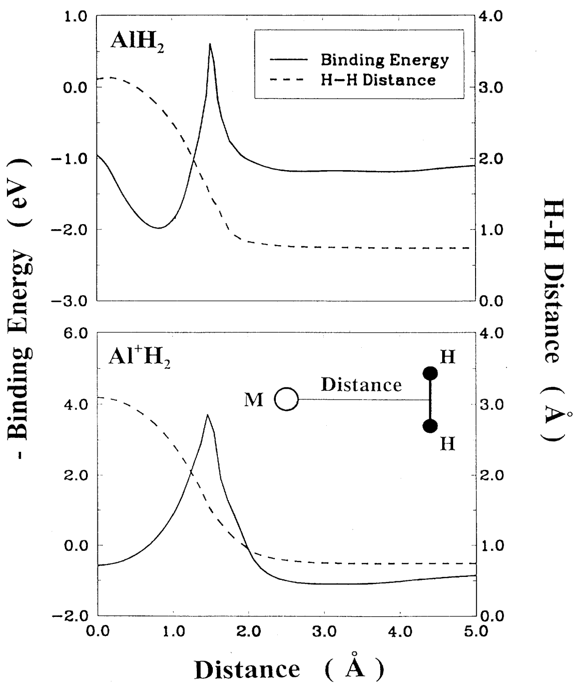

FIG. 1. The binding energy of AlH_2 and $\mathrm{Al}^+\mathrm{H}_2$ as a function of the distance separating the center of mass of the H_2 molecule from the metal atom and cation.

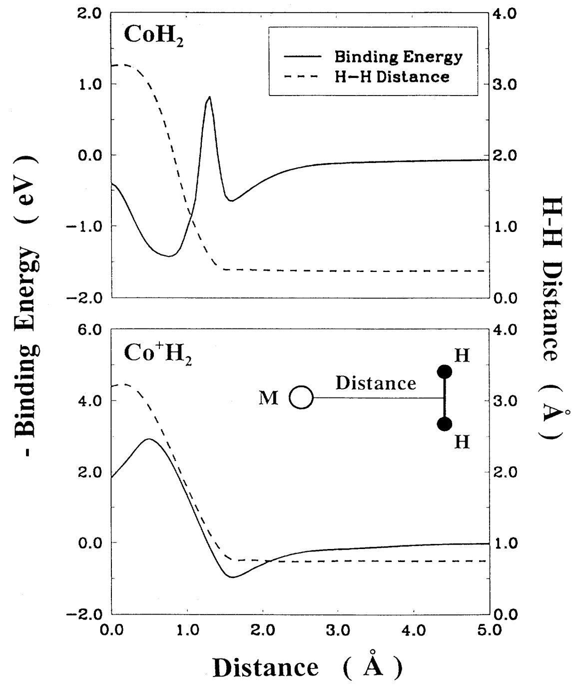

FIG. 2. The binding energy of CoH_2 and $\mathrm{Co}^+\mathrm{H}_2$ as a function of the distance separating the center of mass of the H_2 molecule from the metal atom and cation.

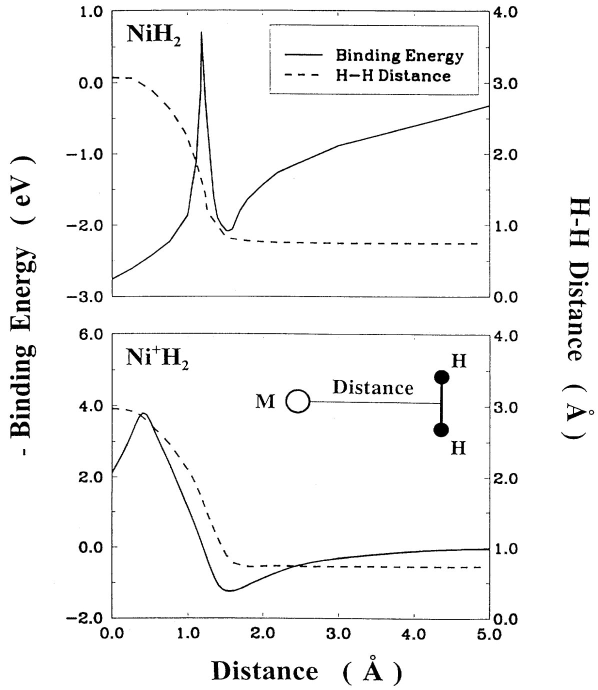

FIG. 3. The binding energy of NiH_2 and $\mathrm{Ni}^+\mathrm{H}_2$ as a function of the distance separating the center of mass of the H_2 molecule from the metal atom and cation.

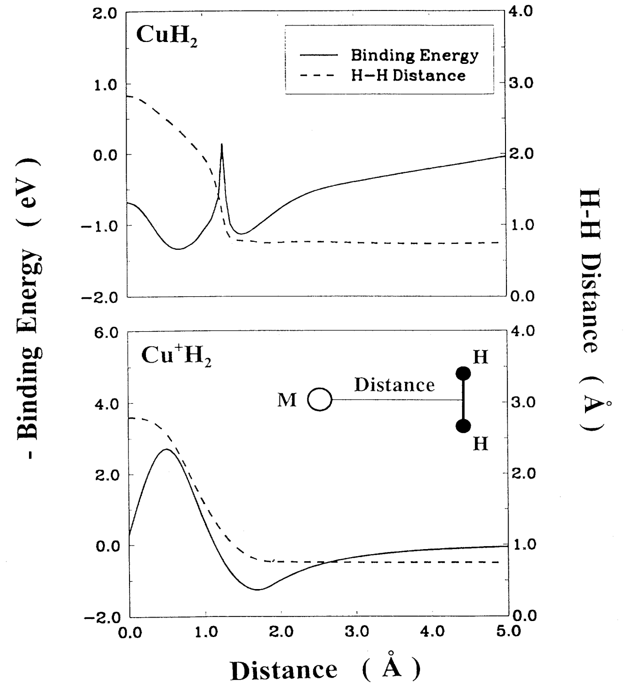

FIG. 4. The binding energy of CuH_2 and Cu^+H_2 as a function of the distance separating the center of mass of the H_2 molecule from the metal atom and cation.

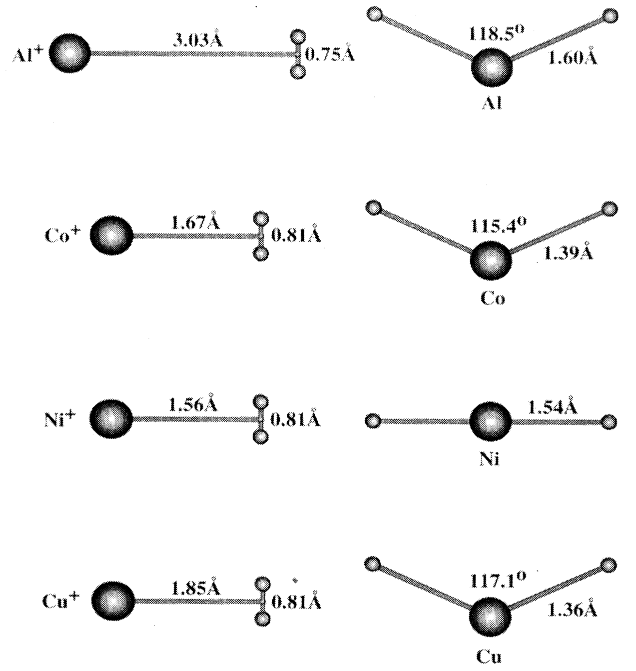

FIG. 5. Equilibrium geometries of H_2 interacting with neutral and positively charged Al, Co, Ni, and Cu atoms.

can be seen from the Mulliken charge analysis in Table IV.

For H_2 interacting with metal cations, the charge transfer to the antibonding state of the H_2 is not possible, since the second ionization potential of the metal atoms is rather high and this energy cost plus that necessary to break the H-H bond cannot be recovered from the H–metal-cation bonds. Thus the bonding takes place associatively, where the electric field produced by the cation polarizes the H_2 molecule and the binding occurs due to the polarization force. We note from Table IV that the binding induced by the polarization force is weaker than that caused by charge transfer. As expected, the H atoms interacting with the metal cations remain in nearly neutral form, as is evident from the Mulliken charge in Table IV. Our result of associative binding of the H_2 molecule to the Co^+ ion as well as the calculated binding energy are in very good agreement with a recent experiment.[19]

It is relevant to mention that the interaction of hydrogen in organometallic complexes has been studied for quite some time using nuclear-magnetic-resonance experiments.[20] In these complexes, the metal atom is bonded to organic ligands and remain in cationic form. It is well known that in these complexes hydrogen atoms exist in

TABLE IV. Binding energies and bond distances for metal atoms and ions interacting with hydrogen molecule.

Type of clusters	Distance, Å X^a-H	Distance, Å H-H	Mulliken population X	Mulliken population H	Binding $\Delta E_{\text{theory}}{}^b$, eV	Binding ΔE_{expt}, eV
Al^+H_2	3.03	0.75	12.018	0.991	1.09	
Co^+H_2	1.67	0.81	26.006	0.997	0.97	0.85±0.04
Ni^+H_2	1.56	0.81	27.170	0.910	1.25	
Cu^+H_2	1.85	0.81	28.004	0.998	1.26	
AlH_2	1.60	2.75	12.848	1.076	1.99	
CoH_2	1.39	2.35	26.094	1.453	1.44	
NiH_2	1.54	3.07	26.274	1.863	2.76	
CuH_2	1.36	2.32	28.564	1.218	1.34	

[a] $X = M, M^+$; M=Al, Co, Ni, Cu.

[b] ΔE is the binding energy defined in theory part.

molecular form. This is consistent with the above description of interaction between H_2 and a metal cation.

The changing nature of the hydrogen binding mechanism from neutral to cationic metal atoms has important consequences for the number of hydrogen atoms that can be bound to a metal atom. For example, it is difficult to bind more than two H atoms to a neutral metal atom, since the latter has only a very limited number of electrons it can transfer with little energy cost. Since for a cation no transfer is necessary and the polarization force decreases as r^{-4} (r being the distance of the H_2 center of mass from the metal cation) and the number of H atoms at a distance r goes as r^3, an infinitely large number of H_2 molecules can be bound to a metal cation at 0 K. Of course, the binding energy per H_2 molecule would decrease as more molecules are added, and it may be very difficult to calculate the binding energy of the last H_2 molecule in a $M^+(H_2)_n$ cluster in the limit of large N.

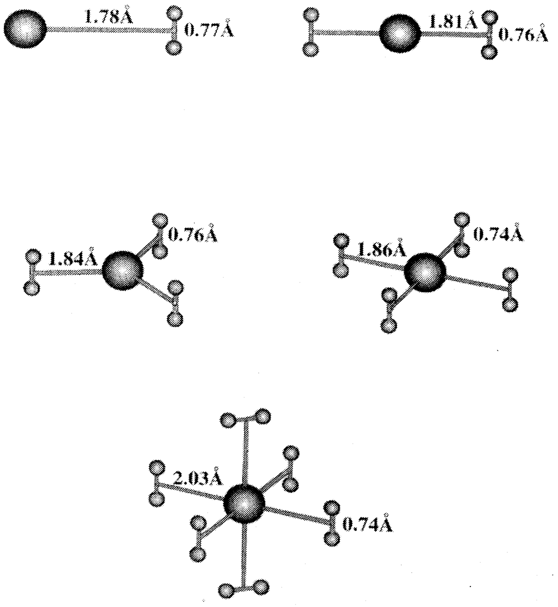

FIG. 6. Equilibrium geometries of $Ni^+(H_2)_n$ cluster for $n \leq 6$.

However, using the method described earlier, we have calculated the binding energy and equilibrium geometry of up to six H_2 molecules around a Ni and Li cation.[21] For this portion of the work it was necessary to reduce the level of the H atomic basis to $(4s\,1p/2s\,1p)$. Although this leads to a small underestimation of the H-H bond, the basic physics remains unchanged. The equilibrium geometries of $Ni^+(H_2)_n$ clusters are given in Fig. 6. The binding energies and Mulliken charges for the constituent atoms in these clusters are listed in Table V. From Fig. 6 we note that the hydrogen atoms remain in molecular form and arrange themselves in shells around the metal cation so as to avoid steric hindrance. The H atoms remain nearly neutral, and H-H bonds approach almost exactly the molecular bond value as more and more H_2 molecules decorate the ion. The interaction of H_2 with Li^+ yields a similar result.[21] In order to examine the nature of H_2 bonding to cluster ions, we have studied the equilibrium geometries and energetics of $Li_2^+(H_2)_n$ clusters. The geometries of these clusters for $n \leq 2$ are given in Fig. 7. We note that H atoms are bound to the Li_2^+ in molecular form as they are to Li^+. The binding energies of $Li_2^+H_2$ and $Li_2^+(H_2)_2$ against dissociation with Li_2^+ and H_2, respectively, are 0.180 and 0.177 eV. These indicate that the binding is caused by charge polarization. As the size n of the metal cluster ion increases, the nature of H_2 interaction must change from associative to dissociative binding. For this critical size of the metal cluster, it should be possible to transfer electrons from the metal cluster to the antibonding state of H_2. It is, however, difficult to determine this critical size since the properties of small metal clusters do not evolve monotonically as size is increased. For example, the binding energies and ionization potentials of alkali- and noble-metal clusters exhibit an odd-even alternation effect.[22] Second, it is not clear whether the size of the metal cluster or the charge density per "surface unit" of the cluster is the relevant parameter. It is quite likely that the critical size for H_2 dissociation may depend on the chemistry of the atoms itself. Since it is the charge transfer from the metal cluster to H_2 that destabilizes the H_2 bond, we believe that the cluster charge-density profile may play a dominant role. Although rigorous calculations are necessary to settle this issue, a qualitative understanding can be achieved by examining the highest occupied molecular-orbital (HOMO) level of a cluster ion. If the level is too low, the charges may be localized, making charge transfer

TABLE V. Results for nickel cation with hydrogen molecules. The basis sets are the same as those in Ref. 15.

Type of clusters	Distance, Å Ni^+-H_2[a]	Mulliken population Ni^+	H	Binding energy per H_2 ΔE_{theory},[b] eV
$Ni^+(H_2)_1$	1.82	27.17	0.91	0.50
$Ni^+(H_2)_2$	1.85	27.27	0.93	0.46
$Ni^+(H_2)_3$	1.88	27.40	0.95	0.36
$Ni^+(H_2)_4$	1.90	27.40	0.95	0.32
$Ni^+(H_2)_6$	2.06	27.60	0.95	0.26

[a] See the geometry for details.

[b] ΔE is the binding energy defined in theory part.

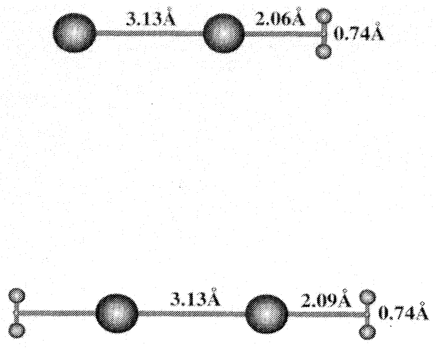

FIG. 7. Equilibrium geometries of $Li_2^+H_2$ and $Li_2^+(H_2)_2$ clusters.

difficult. In Fig. 8 we compare the energy levels of Li_n^+ ($n \leq 5$) with Li^+. Note that the HOMO level of the Li_n^+ ($n=5$) cluster is about -7 eV. It is still so low that we do not expect the H_2 molecules to bind dissociatively even to Li_5^+. We will return to the hydrogen bonding at elevated temperatures and gas densities after we discuss the interaction of metal atoms and cations with He.

C. Binding of He atoms

Unlike the hydrogen atom, the helium atom is characterized by a closed electronic shell. Therefore, it is expected that the binding of He atoms to a transition-metal cation may be caused by the polarization mechanism as described above. The polarizability of the He atom, however, is much less than that of the H_2 molecule, they are 0.205 and 0.8056 Å^3, respectively.[4,23] As a result, one expects the binding energy of He with a metal ion to be lower than that between the H_2 molecule and the metal ion. This is indeed the case, as can be seen from the results in Table VI. The binding energies between He and Co^+, Cu^+, and Ni^+ are typically between 0.1 and 0.15 eV, and the He atoms remain in neutral form. Our calculated binding energies are in good agreement with available experiment.[13,14] Within the accuracy of our calculation, the neutral metal atoms failed to bind to a He atom.

We have also studied the binding of up to six He atoms to a Ni^+ ion. The results are given in Fig. 9 and Table VII. We note that the binding energy is nearly constant, as is the distance between Ni^+ and He as more He atoms are added. This is further proof that the binding between a metal cation and closed-shell system is governed by the polarization mechanism.

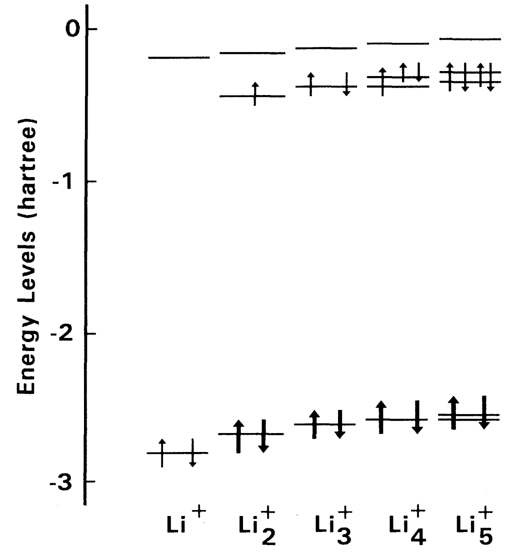

FIG. 8. Energy-level structures of Li_n^+ ($n \leq 5$) clusters.

D. Atkins model for clustering

In the above we have discussed the binding energy of H_2 and He to metal cations at 0 K. Since the binding is caused by the polarization of closed-shell systems, an infinite number of H_2 molecules or He atoms can decorate the cation at 0 K. However, in an experimental situation the number of bound H_2 molecules and He atoms decorating the cation would depend upon the temperature and density of the gas. This problem was studied earlier for the decoration of positive ions passing through liquid He. It was shown that in the thermodynamical equilibrium state the clustering of inert molecules on an ion can be described by a continuum model, where the gas interacts with the electric field of the ion.[12] A molecule at a distance r from the ion will be polarized by an electric field E and have a potential energy

$$V_p = -\tfrac{1}{2}\alpha E^2 = -\frac{\alpha e^2}{2(4\pi\epsilon_0 \epsilon r^2)^2}\ , \tag{4}$$

TABLE VI. Results for metal atoms and ions with helium atom.

Type of clusters	Distance, Å X^a-He$_{\text{theory}}$	X-He$_{\text{expt}}$^{c}	Binding, eV ΔE_{theory}^{b}	ΔE_{expt}^{c}	Mulliken X	He
Al^+He	3.44		0.01		12.004	1.996
Co^+He	1.915	1.180±0.15	0.15	0.131±0.002	26.048	1.952
Ni^+He	1.97	1.80±0.15	0.11	0.129±0.002	27.036	1.964
Cu^+He	1.92		0.16		28.010	1.990

[a] $X = M, M^+$; M=Al, Co, Ni, Cu.
[b] ΔE is the binding energy defined in theory part.
[c] Reference 13.

TABLE VII. Results for nickel cation with helium atoms.

Type of clusters	Distance, Å Ni^+-He[a]	Mulliken population Ni^+	He	Binding energy per He ΔE_{theory},[b] eV
Ni^+He_1	1.97	27.036	1.964	0.110
Ni^+He_2	2.14	27.050	1.975	0.071
Ni^+He_3	2.27	27.052	1.983	0.066
Ni^+He_4	2.36	27.056	1.986	0.068
Ni^+He_5	2.31/2.38[a]	27.075	1.985	0.060
Ni^+He_6	2.39	27.081	1.987	0.056

[a] See the geometry for details.

[b] ΔE is the binding energy defined in theory part.

where α is the polarizability of the gas molecule and ϵ is the dielectric constant of the condensed gas in the cluster. The dielectric constant takes into account the repulsive interaction between the gas molecules due to their polarization. In reality the dielectric constant will depend on the density of the gas in the cluster. For helium the dielectric constant is essentially 1, and for liquid hydrogen it is 1.23.[24] Using the value of r, the equilibrium distance of the center of mass of the first H_2 molecule to the Ni^+ as seen in Fig. 5, we obtain the binding energy of the first H_2 molecule to Ni^+ and Li^+ as 0.5 and 0.3 eV, respectively. These are in good agreement with the *ab initio* results of 0.5 and 0.25 eV if one uses the $(4s1p/2s1p)$ basis for hydrogen. Thus, in the following estimate of the temperature and density dependence of H_2 binding, we use the potential of the form in Eq. (4). In this equation, the polarization potential of the ion will change the chemical potential of the gas as

$$\mu=\mu^{\text{int}}+V_p(r) \ , \tag{5}$$

where μ^{int} is the intrinsic chemical potential. Using the local-density approximation[12,25] for the free energy, the chemical potential is

$$\mu^{\text{int}}(n)=\frac{\partial f(n)}{\partial n} \ , \tag{6}$$

where $f(n)$ is the free energy per unit volume in a homogeneous gas of density n. Far away from the ion, where the potential is zero, the density equals the unperturbed gas density n_0. Consequently,

$$\mu(n_0)=\mu^{\text{int}}(n_0) \ , \tag{7}$$

and Eq. (5) can be written as

$$\mu^{\text{int}}(n_0)=\mu^{\text{int}}(n(r))+V_p(r) \ . \tag{8}$$

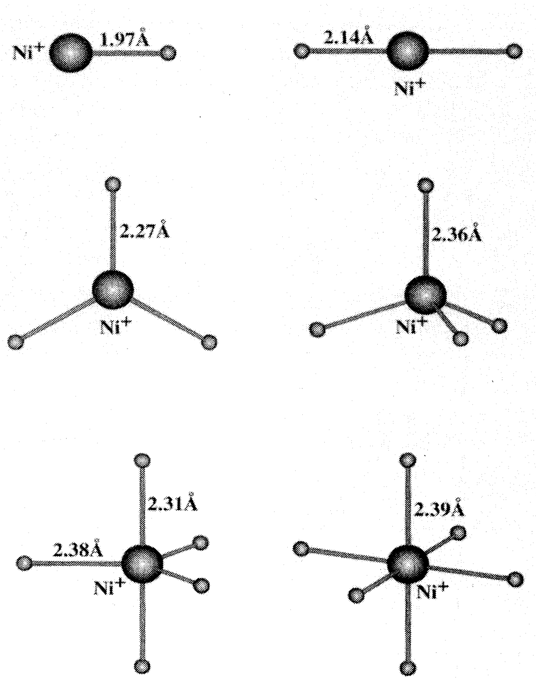

FIG. 9. Equilibrium geometries of $Ni^+(He)_n$ $(n \leq 6)$ clusters.

For simplicity we use the van der Waals equation of state for the gas. This also has the practical advantage that the gas density is limited to a maximum value (a hard-sphere gas), and the divergence of the $1/r^4$ potential does not cause any problems. In the van der Waals model the equation determining the density is[13]

$$\frac{V_p}{k_BT}+\ln\left[\frac{n}{n_0}\right]+\ln\left[\frac{1-n_0b}{1-nb}\right] +\frac{1}{1-nb}-\frac{1}{1-n_0b}-(n-n_0)\frac{a}{k_BT}=0 \ , \tag{9}$$

where a and b are the van der Waals parameters. Standard values are used for a,[24] b,[24] and α.[13,26]

The number of gas molecules clustered around the ion can be estimated by integrating over the induced density:

$$N=\int_{r<r_i} d\mathbf{r}[n(\mathbf{r})-n_0] \ , \tag{10}$$

where r_i is the radius describing the excluded volume due to the ion. This will depend on the ion in question. We have estimated it to be the same as the volume taken by one gas molecule in the dense gas.

The number of molecules attached to the ion at different temperatures and ambient gas densities are shown in Figs. 10 and 11, respectively. For a fixed gas density n, we note that the number of bound hydrogen molecules increases sharply at very low temperatures, and approaches zero asymptotically at very high temperatures. At about 100 K, for example, the number of H_2 molecules bound to a Ni^+ ion is about 6 at a gas density of $1.4\times 29/m^3$. This result agrees well with the recent experimental result[19] in Co^+, where seven H_2 molecules were observed to be bound at 75–120 K. The dependence of bound H_2 molecules on gas density, especially at temperatures higher than 100 K, is not as great as that observed in Fig. 10. However, it should be emphasized that there is an ideal gas density at which a maximum number of H_2 molecules can be bound. These results are based on equilibrium thermodynamics, and do not take into account nonequilibrium conditions related to the dynamics of the gas molecules and/or the transition-metal cluster ions.

Finally, we want to emphasize that the above derivation of the number of molecules attached to a positive ion is only a crude estimate. At high temperatures the number of attached molecules is small and a continuum theory cannot be accurate. The density changes quite rapidly at the surface of the cluster[11] and thus there is no guarantee that the local-density approximation is accurate in that region. Nevertheless, these effects are small compared to the large variation of the number of molecules as a function of the temperature or gas density as shown in Figs. 10 and 11.

IV. CONCLUSIONS

We have demonstrated through self-consistent quantum chemical calculations that the nature of the interaction of H_2 molecules and He atoms with a neutral metal atom is different from that with a metal cation. In the former the binding is caused by transfer of charge from the neutral atom to hydrogen, and the number of H atoms that can be bound to a neutral atom is limited. However, in the case of the ion, the binding is due to the

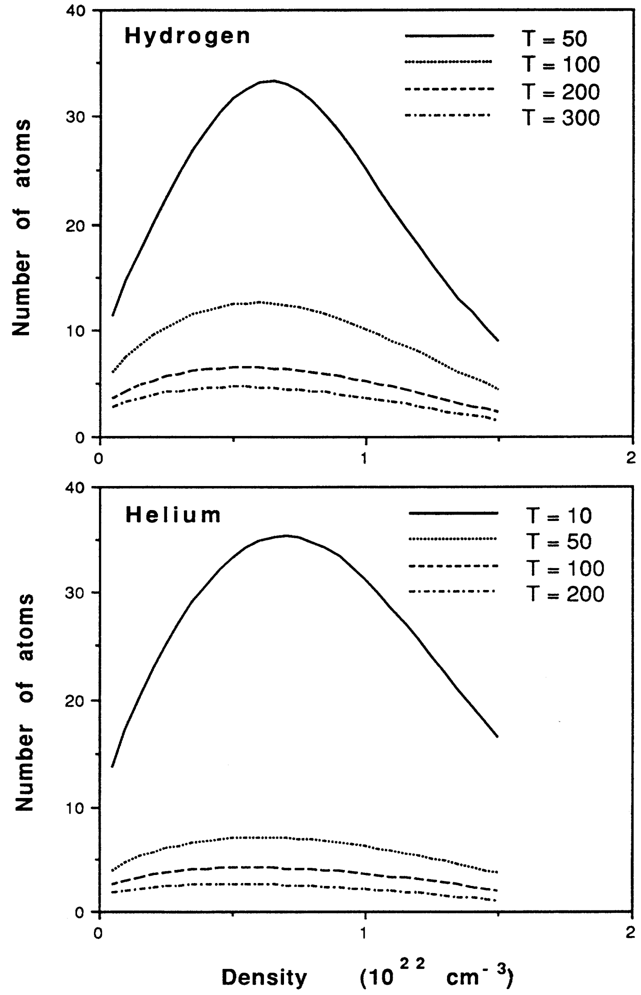

FIG. 10. Dependence of the number of hydrogen molecules and He bound to Ni^+ on the density of the gas at various temperatures.

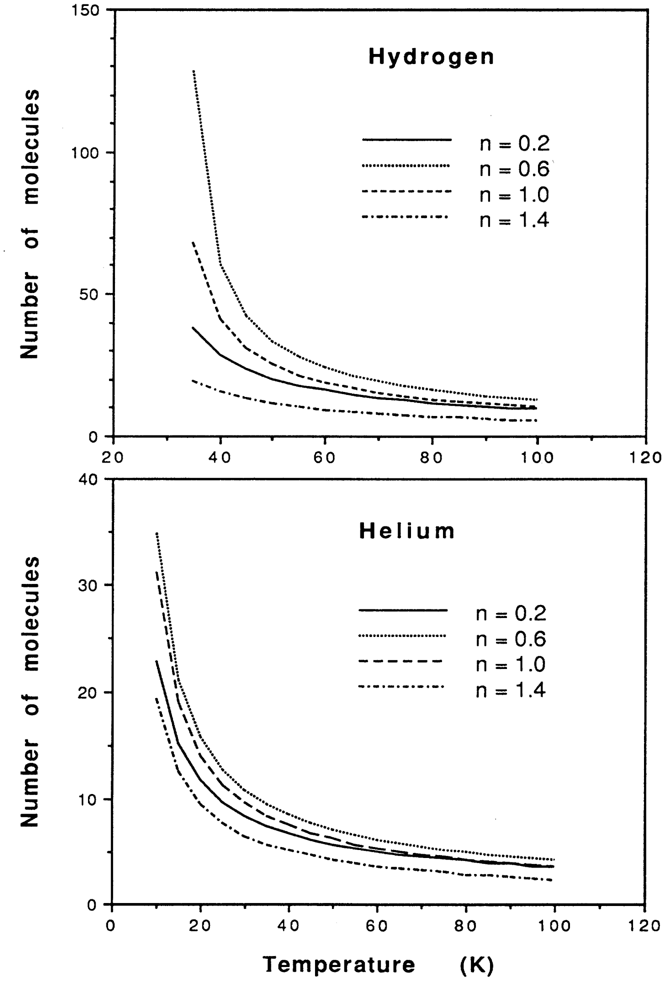

FIG. 11. Dependence of the number of hydrogen molecules and He bound to Ni^+ on the temperature at various gas densities.

polarization of the H_2 molecule. Consequently a large number of H_2 molecules and He atoms can be bound to the ion. The effect of temperature and gas density can put a limit on the number of bound molecules. However, this limit is an order of magnitude larger than what can be achieved by a neutral metal atom.

As the cluster size increases, the charge transfer from cationic clusters to the H_2 molecule becomes easier and, consequently, for certain critical sizes of the cluster the H_2-molecules would dissociate and bind atomically as they do on neutral clusters and metal surfaces. Although this critical size cannot be determined precisely without calculation and is most likely different for different metals, one can obtain an estimate from examining experimental data for the number of H atoms per metal atom in a cluster hydride. Since in most clusters the ratio of H to metal atoms approaches unity for about a 30-atom cluster, one could estimate the critical size of the metal cluster where the nature of hydrogen bonding charges to be around 30. Therefore, it is the small metal clusters that are important for hydrogen binding. It will be worthwhile to isolate small metal clusters in matrices such as zeolites and expose them to hydrogen. If large quantities of hydrogen can be trapped, this system may prove to be useful as a hydrogen storage medium.

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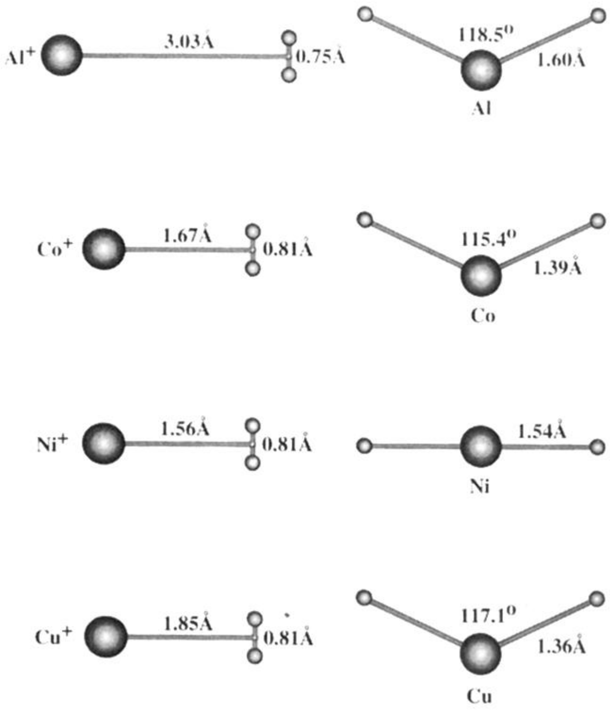

FIG. 5. Equilibrium geometries of H_2 interacting with neutral and positively charged Al, Co, Ni, and Cu atoms.

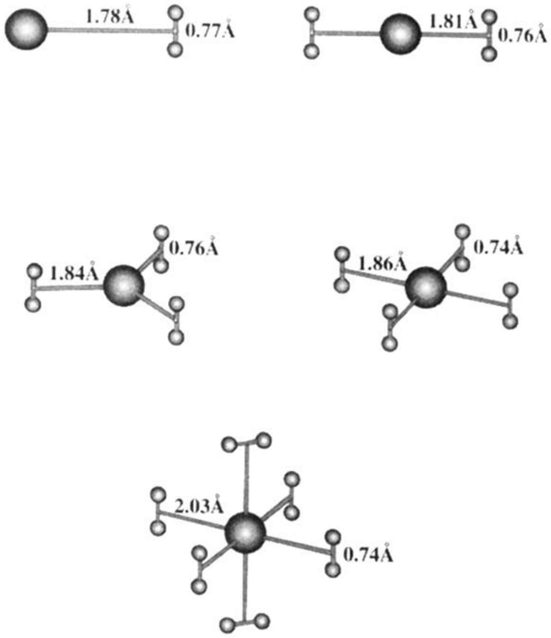

FIG. 6. Equilibrium geometries of $Ni^+(H_2)_n$ cluster for $n \leq 6$.

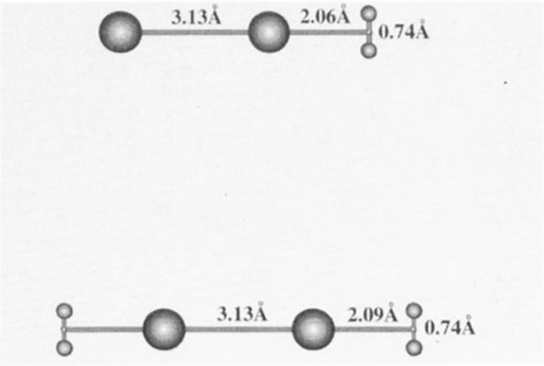

FIG. 7. Equilibrium geometries of $Li_2^+H_2$ and $Li_2^+(H_2)_2$ clusters.

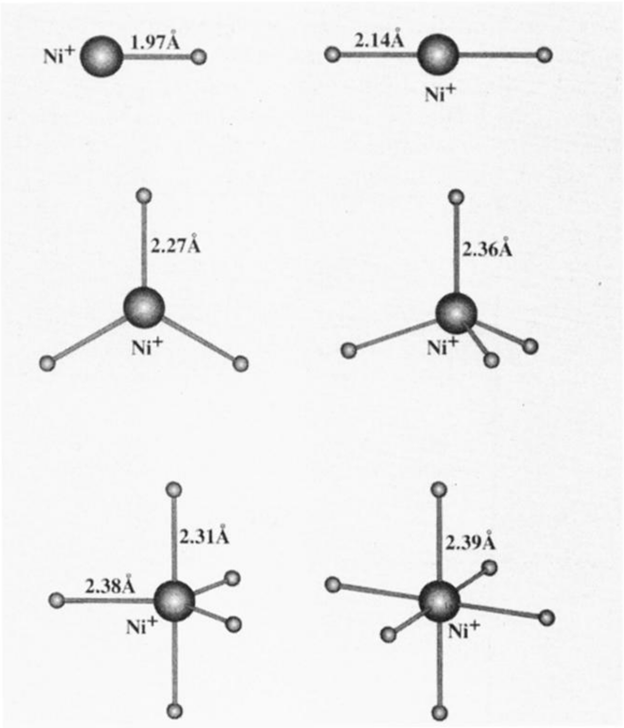

FIG. 9. Equilibrium geometries of $\mathrm{Ni}^+(\mathrm{He})_n$ ($n \leq 6$) clusters.