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$Ni^{+}(H_2)_n$: Ligand bond energies for ground state ions

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Abstract

The H₂ ligand binding energies in Ni⁺(H₂)_n were measured to be 17.3, 17.6, 11.3, 7.1 and 4.2 kcal/mol, for n = 1-5, respectively. The very weakly bound sixth ligand begins a new solvation sphere. Association entropies were also measured. MP2 calculations were done to determine geometries and vibration frequencies as well as the origin of the bonding. The observed changes in BDE with ligation are due to electronic rather than steric effects. Comparisons are made to the Fe⁺(H₂)_n, Co⁺(H₂)_n, Cu⁺(H₂)_n and Ni⁺(CO)_n systems. A highly symmetric D_{3h} planar structure is found in Ni⁺(H₂)₃ and forms the core of the Ni⁺(H₂)_{4.5} ions. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Over the past ten years systematic experiments have examined a large number of gas-phase transition metal ion $M^+ \cdot X_n$ clusters. Relatively simple systems with $X = H_2$ [1–9], CO [10,11], and the rare gases [12], have been examined, as well as saturated and unsaturated hydrocarbons and other species (for a general discussion, see Ref. [13]). The strong influence of the metal ion species on both bond energies and structures in these clusters clearly shows the presence of covalent forces in the bonding. Experimental and theoretical investigations have identified many of these. First, electron donation from the H_2 σ orbital to the metal stabilizes the ion charge ([14,15]; for a general discussion, see Ref. [16]). Most of this donation is to the metal 4s orbital with a minor amount to the $3d\sigma$ orbital. Second, metal ions with filled $3d\pi$ orbitals donate into the H₂ σ^*

orbitals [16,15,17,18]. This promotes σ donation to the ion by returning electron density to the H_2 ligands, and increases the 3d-3d exchange stabilization on the metal. Third, in ions with half filled $3d\sigma$ orbitals, the $3d_{z^2}$ and the 4s orbitals hybridize to reduce on-axis Pauli repulsion [16,15,17-19]. Fourth, the 4p orbitals, while significantly higher in energy, may play a significant role [16-18]. Finally, the non-covalent electrostatic interactions (charge-induced-dipole and charge quadrupole) are present, but usually comprise a small fraction of the total bond strength [1,16,19]. The relative importance of these five factors depends strongly on the valence configuration of the metal ion. The 4s orbital is especially critical and its occupation is always severely destabilizing [6,12,16].

In addition to experimental investigations a large number of theoretical calculations have been done on these $M^+ \cdot X$ systems. The $M^+(H_2)_n$ clusters with M = Fe [7], Co [15,17,18] and Cu [9] have been especially well characterized. These late transition

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metal ions all have relatively strong bond dissociation energies (BDEs) and similar structures for the first and second clusters. Very different structures are found for larger numbers of ligands, however. In the third cluster, both Fe and Co assume a 'T' shape [7,17,18] while Cu has a planar D_{3h} geometry [9]. Both Fe and Co have six H₂ ligands in their first solvation spheres while Cu has four [7,9,17,18].

Nui et al. [20] have examined the Ni⁺(H₂)_{1,2,4,6} ions using an unrestricted Hartree–Fock approach (with correlated valence electrons). Their results for the first two clusters are in general agreement with our findings. Nui et al. predict, however, that Ni⁺ will add between six and ten H₂ ligands — a prediction at odds with previous theoretical and experimental studies of Fe⁺(H₂)_n, Co⁺(H₂)_n and Cu⁺(H₂)_n, and, as will be seen, with the present results. The geometries and bond energies for the larger clusters also disagree with the present results due to the assumption of D_{4h} and O_h symmetries for Ni⁺(H₂)_{4,6} and possibly to the rather small basis sets used.

In this Letter we present experimental association enthalpies and entropies for the sequential clustering of H₂ ligands to ground state Ni⁺ ions. These results are complimented by high-level ab initio calculations that give insight into the bonding mechanisms present. The Ni⁺(H₂)_n clusters will be compared with other late transition metal clusters to illustrate the evolution of the bonding in the series. In addition, the Ni⁺(H₂)_n clusters will be compared with previous results on the Ni⁺(CO)_n ions [11] to evaluate how well bonding concepts transfer from the H₂ to the CO systems.

2. Experimental

Experimental details have been given previously [2,5,21]. Briefly, the Ni⁺ ions were formed either by glow discharge (using an Ar bath gas), by electron impact on Ni(CO)₄ or by surface ionization of Ni(CO)₄. Electronic state chromatography experiments [22] showed that both ground state (²D, 3*d*⁹) and electronically excited Ni^{+*} (^{2,4}F, 4s¹ 3d⁸) were present when the discharge or electron impact sources were used (electron impact ionization produced >

75% excited state [22]). The excited states were resistant to collisional deactivation by H₂ and, because the 4s configuration binds only very weakly to H_2 [6], caused a significant perturbation in the data for the first association. This was ultimately solved by using surface ionization which only forms $\sim 1\%$ excited Ni⁺. After formation, the isotope of interest (either ${}^{58}Ni^+$ or ${}^{60}Ni^+$) is mass selected in the first quadrupole and injected into a drift/reaction cell filled with typically 10 Torr of H₂. An equilibrium between the various Ni⁺(H₂)_n cluster products (n =(0-6) is quickly established as the ions are moved through the 4 cm long cell with a small electric field. The field is small enough that no measurable perturbation of the thermodynamic temperature occurs. The ions then exit the cell and are mass analyzed in a second quadrupole. The resulting mass peaks are recorded and integrated and, together with the pressure of $H_2(p_{H_2})$ and the temperature (T) are used to calculate the equilibrium constant (K_p) and standard free energy (ΔG_T°)

$$K_{p}^{o} = \frac{\mathrm{Ni}^{+}(\mathrm{H}_{2})_{n}^{*}760}{\mathrm{Ni}^{+}(\mathrm{H}_{2})_{n-1}^{*}p_{\mathrm{H}_{2}}},$$
(1)

$$\Delta G_T^{\circ} = -RT \ln K_p^{\circ}. \tag{2}$$

Measurements were taken as a function of temperature from 77 to 780 K. The resulting plots of ΔG_T^o vs. *T* were linear over the experimental temperature range, yielding ΔH_T^o and ΔS_T^o as the intercept and slope, respectively. To determine the heat of reaction at 0 K (ΔH_0^o), the experimental ΔG_T^o vs. *T* curve is matched with a corresponding theoretical curve calculated using the theoretically determined structures and vibrational frequencies. The low vibrational frequencies and possible mass discrimination are varied to determine the value and uncertainty in the bond dissociation energy (BDE = $-\Delta H_0^o = D_0$) [23].

3. Theoretical methods

The product ions discussed here were all examined theoretically both to determine the molecular parameters needed to analyze the experimental data and to identify factors important in the bonding. Calculations were carried out at the MP2 level [24] using the TURBOMOLE package [25]. The hydrogen basis set was the 'SVP' set [26]. For the nickel basis set we used the 'ECP-10-MDF' which includes a pseudo-potential to describe the core electrons [27].

4. Results and discussion

Fig. 1 shows the experimental ΔG_T° vs. *T* data. The experimental enthalpies and entropies for the association reactions are summarized in Table 1 along with theoretical binding energies for both ground and excited state cluster ions. Calculated vibrational frequencies are listed in Table 2. Structures of the various Ni⁺(H₂)_n ions are shown in Fig. 2. Finally, Table 3 compares BDEs for the first-row transition metal ion M⁺(H₂)_n complexes.

4.1. $Ni^+(H_2)$

The Ni⁺H₂ complex has an experimental BDE of 17.3 kcal/mol. This is similar to that found with the

 $3d^n$ complexes of Fe⁺(H₂) and Co⁺(H₂) (17.8 and 18.2 kcal/mol, respectively) but somewhat greater than that of $Cu^+(H_2)$ (15.4 kcal/mol, see Table 3). Our calculated BDE is 15.6 kcal/mol, or $\sim 90\%$ of the experimental value. The cluster structure is nearly identical to that of the other late metals: all have C_{2n} symmetry and an M^+ – H_2 bond length of ~ 1.65 Å. We might expect that both the electrostatic and covalent attractions in $Cu^+(H_2)$ would be larger due to the slightly smaller ionic radius [28,29]; however, the Ni⁺(H₂) BDE is actually ~ 15% greater. The origin of the lower bond strength in $Cu^+(H_2)$, a $3d^{10}$ ion, is the filled $3d_{z^2}$ (d σ) orbital on Cu⁺ which destabilizes the complex. In both $Co^+(H_2)$ and $Ni^+(H_2)$ the H₂ approaches a half-filled $3d_{z^2}$ orbital and calculations indicate $3d\sigma/4s$ hybridization reduces the M^+-H_2 repulsion by moving the z axis electron density to the xy plane [16–19]. This hybridization is a higher-energy process in Cu⁺ due to the necessity of moving two electrons and the resulting bond is weaker [9].

Binding energies were also calculated for the excited states of $Ni^+(H_2)$ which correspond to mov-



Fig. 1. Plot of experimental ΔG_T^o vs. temperature for the association reaction Ni⁺(H₂)_{*n*-1} + H₂ \rightarrow Ni⁺(H₂)_{*n*}. Open symbols refer to electron impact data (~75% electronically excited Ni^{+*}), closed symbols refer to surface ionization data (99% ground state Ni⁺). The excited Ni^{+*} only affects the data for the first association.

ing the electron hole in ground state Ni⁺ (²D, 3d⁹) to one of the other five 3d orbitals (Table 1). When the 3d_{xy} (3d δ) is half filled, the BDE is reduced by ~ 1.5 kcal/mol. As expected, this corresponds closely to the BDE for Cu⁺(H₂) since the M⁺-H₂ interactions are now very similar. A major reduction in BDE (7.7 kcal/mol) occurs when the back bonding 3d π is half filled (the ²B₁ state), showing the importance of this interaction. As expected, the BDE is now similar to the early metals (Table 3).

The Ni⁺(CO)_n ions have been investigated both experimentally and theoretically and exhibit bonding very similar to those in Ni⁺(H₂)_n [11,30]. The carbon σ orbital donates into the Ni⁺ 4s orbital while the filled Ni⁺ d π orbitals (3d_{xz} and 3d_{yz}) donate into the CO p π^* orbitals. Hybridization of the Ni⁺ 4s and 3d σ orbitals is used to reduce Pauli repulsion. Again, the σ and π dative interactions are synergistic: the π donation makes the CO more negative and thus better able to donate into the M⁺ 4s orbital. The strength of the Ni⁺-CO bond is much greater than that of Ni⁺H₂ (41.711 vs. 17.3 kcal/mol) at least partly due to the presence of two π interactions

Table 1				
Data summary	for	Ni ⁺	$(H_{2})_{n}$	clusters

instead of one. Both $M^+(CO)$ and $M^+(H_2)$ show similar trends as the M^+ ion is changed from Co⁺ to Ni + to Cu⁺, but the M^+-H_2 bond strengths are ~40-45% of the M^+CO values.

4.2. Ni⁺ $(H_2)_2$

The second H₂ ligand binds opposite the first in D_{2h} symmetry with a measured BDE of 17.6 kcal/mol. The calculated bond lengths are nearly identical to those in $Ni^{+}(H_{2})$, reflecting the similarity in bonding (Fig. 2). The second BDE is 0.3 kcal/mol larger than that of the first cluster, however, due to the benefit of the symmetric $4s/3d\sigma$ hybridization which occurred with the first H₂ addition [19]. The D_{2d} structure is calculated to be 0.8 kcal/mol higher in energy than the D_{2h} despite the fact that in D_{2h} symmetry back donation to both ligands is from a single π -type orbital (d_y). In both $Co^+(H_2)_2$ and $Cu^+(H_2)_2$ the D_{2h} states are higher in energy (~ 0.7 and ~ 0.3 kcal/mol, respectively). This reverse preference is also present in $V^+(H_2)_2$ $(3d^4, D_{2h})$ and may be due to the availability of a

Ion	Experiment	Experiment				Theory		
	$\overline{\Delta H_0^{\mathrm{o}\mathrm{a}}}$	$-\Delta H_T^{\mathrm{o}\mathrm{a}}$	$-\Delta S_T^{ob}$	T ^c	symmetry ^d	$D_{\rm e}^{~\rm d}$	D_0^{d}	
Ni ⁺ (H ₂)	17.3 ± 0.3 ^e	18.7 ± 0.5	20.7 ± 2	650 ± 90	$\begin{array}{c} C_{2v} \ {}^{2}A_{1} \\ ex. \ {}^{2}A_{2} \\ ex. \ {}^{2}B_{1} \\ ex. \ {}^{2}B_{2} \end{array}$	17.9 16.5 10.2 13.1	15.6	
$Ni^{+}(H_{2})_{2}$	$17.6 \pm 0.3^{\text{e}}$	18.0 ± 0.4	24.1 ± 2	575 ± 175	$egin{array}{c} D_{2h} \ D_{2d} \end{array}$	19.4 18.6	15.5	
$Ni^{+}(H_{2})_{3}$	$11.3 \pm 0.3^{\text{e}}$	11.7 ± 0.4	23.5 ± 2	425 ± 175	D _{3h} plan. ^f	14.1	9.6	
$Ni^{+}(H_{2})_{4}$	$7.1 \pm 0.3^{\rm e}$	8.7 ± 0.6	24.5 ± 2	300 ± 120	C_s pyr. D_{4h} vert. ^f	10.7 4.8	7.1	
$Ni^{+}(H_{2})_{5}$	$4.2\pm0.2^{\mathrm{e}}$	4.9 ± 0.4	22.5 ± 2	180 ± 70	Cs bipyd.	5.3	3.2	
$Ni^{+}(H_{2})_{6}$	$0.8\pm0.2^{\mathrm{g}}$	0.9 ± 0.2	10.0 ± 2	120 ± 40	D _{2h}	-8.5 ^{e, h}	_	

^aIn kcal mol⁻¹.

^bIn cal mol⁻¹ K⁻¹.

^cIn kelvin (\pm refers to temperature range, not uncertainty).

^dMP2 geometries.

^eFitting with theoretical frequencies and geometries.

^fThe H–H bonds are all either perpendicular (vert.) or parallel (plan.) to the σ_h plane.

^gFitting with ΔC_p correction (error small at low temperature).

^hSixth H₂ is unbound in first solvation shell.

second ²A_a state to mix with the ground state in D_{2h} symmetry (absent in D_{2d} symmetry).

The Ni⁺(CO)₂ ion is also linear but, unlike the in H₂ case, the second CO BDE is slightly weaker than the first (40.1 vs. 41.7 kcal/mol [11]). In both the first and second clusters, however, the Ni⁺-H₂ bond strength is 42 + 2% of the corresponding CO BDE.

4.3. Ni⁺ $(H_2)_3$

The observed bond dissociation energy for the third H_2 ligand is 11.3 kcal/mol (Table 1). This represents a decrease in average BDE from 17.4 to 15.4 kcal/mol. The optimized MP2 structure for the $Ni^{+}(H_2)_3$ ion has D_{3h} symmetry with all atoms in the xy plane (Fig. 2). This same structure is found in $Cu^{+}(H_{2})_{3}$ and as discussed previously, both the highly symmetric structure and the marked decrease in bond strength are mainly due to the repulsive interaction of the H₂ σ orbitals with the 3d shell on Cu^+ and Ni⁺. In the planar D_{3h} structure, the three H_2 ligands have a repulsive σ interaction with three of the Ni⁺3d orbitals $(3d_{2}(a_{1}))$ and $3d_{x^2-y^2}/3d_{yy}(e')$, the z axis is the symmetry axis). The ion reduces this repulsion in two ways. First, the 4s and 3d₂ orbitals hybridize to move electron density from the xy plane to the +z lobes. Second, and more important, the Ni⁺ ion donates electron density from the repulsive $3d_{r^2-v^2}/3d_{rv}(e')$ pair of orbitals to the three $H_2 \sigma^*$ orbitals. This pair of orbitals is symmetry adapted to produce both two repulsive σ interactions and two attractive π interactions with the three ligands. The resulting π back donation is similar to that in the first two clusters, but in the third cluster the back donation also reduces the σ repulsion. This 'push-pull' mechanism has the effect of greatly increasing the extent of back donation while at the same time reducing σ repulsion and is the primary driving force for the D_{3h} structure. The large increase in H-H bond length (Fig. 2) and reduction in H_2 vibrational frequency (Table 2) show the presence of increased back donation in the third cluster.

The second (vertical) D_{3h} structure, with the H_2 ligands perpendicular to the xy plane, is higher in energy and is actually a transition state. This might seem surprising since the vertical and planar D_{3h} forms have nearly identical σ repulsion and each has

Table 2				
Theoretical vi	brational frequencies for Ni ⁺ (H $_2$	$_{2})_{n}$ clusters ^{a,b}		
Ion	H-H stretch	Asym. M ⁺ –H ₂ stretch	Sym. M ⁺ -H ₂ stretch	$H_2 - M^+ - H_2$ bends and rotations
$Ni^+(H_2)$	3835	1378	874	
$Ni^+(H_2)_2$	3861, 3840	1401, 1386	1009, 899	434, 372, 189
$Ni^{+}(H_{2})_{3}$	3604(2), 3603	1450(2), 1444	983, 971(2)	635, 611(2), 429, 378(2)
$Ni^{+}(H_{2})_{4}$	4178, 3648, 3645, 3616	1429, 1416, 1412, 1098	964, 948, 945, 730	$590, 560, 550, 454, 443, 415, 398, 391, -68^{\circ}$
$Ni^{+}(H_{2})_{5}$	4261(2), 3666, 3664, 3654	1405, 1401, 1400, 938, 937	900, 889, 888 , 660, 597	570, 570, 558, 554, 486, 414, 413, 367, 351, 306, 82, 21
H ₂	4515			
All numbers	in1			

³All numbers in cm⁻¹. ⁹Frequencies in bold refer to the Ni⁺(H₂)₃ D_{3h} core.

Structure optimized to better than 1 µhartree; the negative frequency is associated with the very loose orientation of the fourth H₂ ligand.

a degenerate pair of d orbitals available for back bonding (either the e" or e' set). Further, the vertical isomer has lower ligand–ligand repulsion (although this is negligible). The destabilization of the vertical D_{3h} cluster is due to the loss of the very beneficial 'push–pull' mechanism present in the planar geometry since back donation from the e" pair of orbitals does not lead to any reduction in σ repulsion. The relative stabilities of the planar D_{3h} geometries (found in Ni⁺(H₂)₃ and Cu⁺(H₂)₃) and the asymmetric 'T' structures (in Fe⁺(H₂)₃ and Co⁺(H₂)₃) have been discussed previously [9].

A very similar reduction in BDE is found between the Ni⁺(CO)₂ and Ni⁺(CO)₃ [11]. Although no calculations have been done on Ni⁺(CO)₃, a D_{3h} ground state is found in the iso-electronic Fe⁻(CO)₃ ion [31].

4.4. Ni⁺
$$(H_2)_4$$

The fourth H_2 'caps' the planar third cluster to form a distorted trigonal pyramid. The symmetry is C_s , and Fig. 2 shows that the three equatorial ligands are strongly bound while the polar ligand is much more weakly attached. There is little change in the



Fig. 2. Theoretical geometries of the Ni⁺(H₂)₁₋₅ ions calculated at the MP2 level. All distances are in angtröm.

Table 3

 $M^+(3d^n)$: comparison of binding energies^a for $M^+(H_2)_{n-1} + H_2 \rightarrow M^+(H_2)_n$

	-	"						
n	Ti ⁺	V^+	Cr^+	Fe ⁺	Co^+	Ni ⁺	Cu ⁺	
1	10.0 ^b	10.2	7.6	16.5 ^c	18.2	17.3	15.4	
2	9.7	10.7	9.0	15.7	17.0	17.6	16.7	
3	9.3	8.8	4.7	7.5	9.6	11.3	8.8	
4	8.5	9.0	3.4	8.6	9.6	7.1	5.1	
5	8.2	4.2	1.4	2.2	4.3	4.2	1.0 ^d	
6	8.7	9.6 ^e	1.1	2.3	4.0	0.8 ^d	1.0	

^aIn units of kcal mol⁻¹.

^bBinding energy with respect to lowest d³ configuration.

^cBinding energy with respect to lowest d⁷ configuration.

^dStart of next solvation sphere.

^eThe increase in $-\Delta H_0^{\circ}$ for n = 6 is due to a spin change from quintet to triplet on the core V⁺ ion (see Refs. [4,16]).

Ni⁺-H₂ or H–H bond lengths of the equatorial H₂ ligands between the third and fourth clusters and the very stable D_{3h} core is largely preserved. The experimental BDE is 7.1 kcal/mol, which is 8.3 kcal/mol less than the three equal 15.4 kcal/mol bonds in the third cluster. The decrease is due primarily to increased σ repulsion from the 3d_{z²} orbital. Remember that in the third cluster 4s/3d hybridization was used to reduce σ repulsion by moving the 3d_{z²} equatorial electron density to the ±*z* poles. This same hybridization now works to greatly increase repulsion toward the fourth H₂ ligand and a lower BDE results.

This structure is unique among the transition metal-H₂ complexes. The $Cu^+(H_2)_4$ ion has a quasi-tetrahedral geometry with four nearly equal bonds. The Ni⁺(H₂)₄ geometry (capped D_{3h}) is unstable in Cu⁺ due to the increased repulsion from the filled $3d_{2}$ orbital. Both $Fe^{+}(H_{2})_{4}$ and $Co^{+}(H_{2})_{4}$ have 'butterfly' structures with two strongly bound ligands on the z axis and two more weakly bound on the x and y axes [7,17,18]. This is due to the larger number of half-filled orbitals which stabilize the side-on ('T') geometry relative to the planar D_{3h} in the third and fourth clusters. The Ni⁺(H₂)₃ D_{3h} geometry is actually unstable in $Fe^+(H_2)_3$ and $Co^+(H_2)_3$ due to an unequal occupation of the e' orbital set which causes a Jahn-Teller distortion of the D_{3h} symmetry. These effects have been discussed in detail previously [9].

The BDE of $Ni^+(CO)_4$ is also much lower than $Ni^+(CO)_3$ [11] but no calculations on these ions have

been done. However, the isoelectronic $Fe^{-}(CO)_4$ ion is formed by capping the planar $Fe^{-}(CO)_3$ ion [31].

4.5. Ni⁺(H_2)₅

Our MP2 calculations show the Ni⁺(H₂)₄ ion ground state to be a trigonal bipyramid (Fig. 2) with two weakly bound polar H₂ ligands capping the planar Ni⁺(H₂)₃ core group. Both the bond lengths and the H_2 vibrational frequencies (Table 2) show that the $Ni^+(H_2)_3$ core is largely unchanged from the third cluster, indicating again that this structure is extremely stable. The BDE of the fifth H_2 is 4.2 kcal/mol, down form the 7.1 kcal/mol in the fourth cluster. This is partly due to destabilization of the $Ni^{+}(H_2)_3$ core (the $Ni^{+}-H_2$ bond lengths increase very slightly, ~ 0.01 Å) but it is the fourth H_2 ligand which seems to be most affected (here the Ni^+H_2 bond length increases 0.13 Å). We speculate that the 4p₂ orbital is used in the fourth cluster to polarize the z axis electron density away from the polar H₂ ligand as in Fe⁻(CO)₄ [31]. This mechanism is counter-productive when the fifth H₂ ligand is added opposite the fourth, and a reduction in BDE occurs.

The fifth addition closes the first solvation sphere for the Ni⁺(H₂)_n clusters. Both Fe⁺ and Co⁺ (as well as all the early transition metal ions) add six H₂ ligands in their first solvation shell while Cu⁺ adds four. The determining factor is the occupation of the Cartesian orbital set (the $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals) [9]. If these orbitals are each empty or half filled, octahedral occupation occurs; as the set is filled, σ repulsion increases and the first shell occupation is reduced to five (Ni⁺(H₂)₅) or four (Cu⁺(H₂)₄).

4.6. Ni⁺(H_2)₆

Both the extremely weak BDE (0.8 kcal/mol) and, especially, the very small ΔS_T° show that the sixth ligand is added in the second solvation shell. The very low vibrational frequencies, free H₂ rotations and large rotational moments which result all give rise to more product entropy and make the ΔS_T° of association more positive (-10.5 cal mol⁻¹ K⁻¹ vs. -24 to -21 cal mol⁻¹ K⁻¹ for the first five association reactions, see Table 1). The lowest energy first solvation shell structure for Ni⁺(H₂)₆ is calculated to be octahedral (as in $\text{Co}^+(\text{H}_2)_6$); however, this structure is unbound with respect to the separated reactants (Table 1).

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References

- J.E. Bushnell, P.R. Kemper, M.T. Bowers, J. Phys. Chem. 98 (1994) 2044.
- [2] J.E. Bushnell, P.R. Kemper, P. Maître, M.T. Bowers, J. Am. Chem. Soc. 116 (1994) 9710.
- [3] J.E. Bushnell, P.R. Kemper, P. Maître, M.T. Bowers, J. Chem. Phys. 106 (1997) 10153.
- [4] J.E. Bushnell, P.R. Kemper, M.T. Bowers, J. Phys. Chem. 97 (1993) 11628.
- [5] P.R. Kemper, P. Weis, M.T. Bowers, Int. J. Mass Spectrom. Ion Phys. 160 (1997) 17.
- [6] P. Weis, P.R. Kemper, M.T. Bowers, J. Phys. Chem. A 101 (1997) 2809.
- [7] J.E. Bushnell, P.R. Kemper, M.T. Bowers, J. Phys. Chem. 99 (1995) 15602.
- [8] P.R. Kemper, J. Bushnell, P.A.M. van Koppen, M.T. Bowers, J. Phys. Chem. 97 (1993) 1810.
- [9] P.R. Kemper, P. Weis, P. Maître, M.T. Bowers, J. Am. Chem. Soc. (submitted).
- [10] F. Meyer, Y.-M. Chen, P.B. Armentrout, J. Am. Chem. Soc. 117 (1995) 4071, and references therein.
- [11] F.A. Khan, D.L. Steele, P.B. Armentrout, J. Phys. Chem. 99 (1995) 7819.

- [12] P.R. Kemper, M.-T. Hsu, M.T. Bowers, J. Phys. Chem. 95 (1991) 10600.
- [13] B.S. Freiser (Ed.), Organometallic Ion Chemistry, Kluwer, Dordrecht, 1996.
- [14] P. Maître, C.W. Bauschlicher, J. Phys. Chem. 99 (1995) 6836.
- [15] P. Maître, C.W. Bauschlicher, J. Phys. Chem. 97 (1993) 11912.
- [16] C.W. Bauschlicher, H. Partridge, S.R. Langhoff, in: B.S. Freiser (Ed.), Organometallic Ion Chemistry, Kluwer, Dordrecht, 1996.
- [17] P. Maître, C.W. Bauschlicher, J. Phys. Chem. 99 (1995) 3444.
- [18] J.K. Perry, G. Ohanessian, W.A. Goddard, J. Phys. Chem. 97 (1993) 5238.
- [19] H. Partridge, C.W. Bauschlicher, S.R. Langhoff, J. Phys. Chem. 96 (1992) 5350.
- [20] J. Niu, B.K. Rao, P. Jena, Phys. Rev. Lett. 68 (1992) 2277.
- [21] P.R. Kemper, M.T. Bowers, J. Am. Soc. Mass Spectrom. 1 (1990) 197.
- [22] M.T. Bowers, P.R. Kemper, G. von Helden, P.A.M. van Koppen, Science 260 (1993) 1446.
- [23] P.R. Kemper, M.-T. Hsu, M.T. Bowers, J. Phys. Chem. 95 (1991) 10600.
- [24] C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618.
- [25] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165.
- [26] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 97 (1992) 2571.
- [27] M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys. 86 (1987) 866.
- [28] L.A. Barnes, M. Rosi, C.W. Bauschlicher, J. Chem. Phys. 93 (1990) 609.
- [29] P. Desclaux, At. Data Nucl. Data Tables 12 (1973) 312.
- [30] L.A. Barnes, M. Rosi, C.W. Bauschlicher, J. Chem. Phys. 93 (1990) 609.
- [31] A. Ricca, C.W. Bauschlicher, J. Phys. Chem. 99 (1995) 5922.