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Theoretical Studies of Transition-Metal Hydrides. 1. Bond Energies for MH$^+$ with M = Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn

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Abstract: We present here consistent ab initio calculations (generalized valence bond plus configuration interaction) on the 11 molecules MH$^+$ with M = Ca through Zn. The ground-state symmetry, bond distance, vibration frequency, and bond energy are reported. The character of the wave function is used to analyze the bond energy and to rationalize the ground-state symmetry and spectroscopic properties. Excellent agreement (average error = 3.5 kcal) is found with recent experimental bond energies.

In order to understand the bonding in transition metals, it is important to disentangle several competing terms: (a) the relative *intrinsic strength* of bonding to metal s and d orbitals, (b) additional *hybridization* stabilization resulting from mixing of s, p, and d orbitals, (c) the *availability* of the optimal-bonding orbital or combination of orbitals (it is sometimes necessary to excite the atom to obtain the optimum orbital), and (d) the role of *atomic-exchange* energies[1] in moderating the intrinsic bond energy. Because of the large amount of experimental data becoming available,[2-9] systematic theoretical studies on transition metal hydride cations, MH$^+$, would be most valuable. Toward this end we have carried out a sequence of consistent ab initio calculations on the 11 transition-metal systems from CaH$^+$ to ZnH$^+$. Here we report the spectroscopic properties for the ground states of systems at the highest level of calculation; a subsequent paper will present further results on excited states and the results for lower levels of calculation.

Calculational Details

All calculations involve all-electron ab initio wave functions with a basis consisting of an optimized valence double-ζ contraction on the metal[10](5 d primitives) and the Dunning/Huzinaga double-ζ basis[11] for H (4s/2s) supplemented with one set of p polarization functions optimized for MnH$^+$ ($\zeta = 0.50$). The starting point for each calculation was a generalized valence bond (GVB) wave function with the valence bond spin eigenfunction [GVB-PP-(1/2)].[12] Several higher-order calculations were carried out, each designed to dissociate properly to the comparable level calculation on the atoms. These higher-order calculations are based on the procedures developed by Bair and Goddard[13] and denoted as GVB-DCCI (for dissociation-consistent configuration interaction).

The bond dissociation energy calculations involved starting with the three configurations implied by the GVB wave function and allowing all double excitations out of the bond pair *simultaneous with* all single excitations out of the other nonbonding valence orbitals. At $R = \infty$, this dissociates to a limit involving simultaneous single excitations out of the nonbonding orbitals and the metal σ orbital (the one associated with the bond). For various C–H, N–H, O–H, and F–H bonds, Bair and Goddard[13] found that this procedure leads to bond energies about 3 kcal smaller than the experimental. We anticipate similar accuracy for MH$^+$ and indeed find an average error of 3.5 kcal.

Table I. Character of Wave Functions for MH$^+$ from GVB Calculations[a]

molecule	state	character of metal bonding orbital % s	% p	% d	overlap	charge transfer to H
CaH$^+$	$^1\Sigma$	60.0	16.3	23.7	0.749	0.19
ScH$^+$	$^2\Delta$	46.2	13.5	40.3	0.763	0.22
TiH$^+$	$^3\Phi$	46.6	14.7	38.7	0.755	0.08
VH$^+$	$^4\Delta$	48.5	14.1	37.4	0.753	0.07
CrH$^+$	$^5\Sigma$	40.6	12.5	46.9	0.734	0.07
MnH$^+$	$^6\Sigma$	76.3	12.5	11.3	0.718	0.08
FeH$^+$	$^5\Delta$	73.1	12.8	14.1	0.732	0.06
CoH$^+$	$^4\Phi$	74.5	12.1	13.4	0.730	0.03
NiH$^+$	$^3\Delta$	76.5	11.0	12.5	0.726	0.02
CuH$^+$	$^2\Sigma$	70.2	10.5	19.3	0.750	0.03
ZnH$^+$	$^1\Sigma$	90.7	8.9	0.4	0.690	0.07
av	Ca–Zn				0.73	0.08
	Ca–Cr	48	14	38		
	Mn–Cu	74	12	14		

[a] All results based on the GVB-PP wave function.

The equilibrium geometry and vibrational frequencies were determined at a slightly lower level of calculation. This involved starting with the three configurations of the GVB wave function and allowing all double excitations from the bond pair *plus* all single excitations out of the nonbonding valence orbitals. This dissociates to single excitations from the nonbonding orbitals on the metal ion.

Results

A. Character of the Wave Function. All MH$^+$ bonds are quite covalent, with an average of 0.08 e$^-$ transferred from M$^+$ to H. The GVB bond pair involves one electron in an orbital mainly localized on the H and one electron in an orbital mainly localized on the M$^+$, as indicated in Figure 1. The overlap of this GVB pair averages 0.73, typical for a strong covalent bond. For CaH$^+$ through CrH$^+$, there are zero to four nonbonding electrons, and the ground state has all nonbonding electrons in π or δ orbitals. In this case, the bond orbital on M$^+$ has a significant amount of dσ character (the average is 48% 4s, 14% 4p, and 38% 3dσ), as indicated in Table I. However, for MnH$^+$ through CuH$^+$ there are five to nine nonbonding electrons, leading always to one nonbonding electron in dσ. In this case the M$^+$-like orbital of the bond pair is nearly 4s-like (74% 4s, 12% 4p, and 14% 3dσ).

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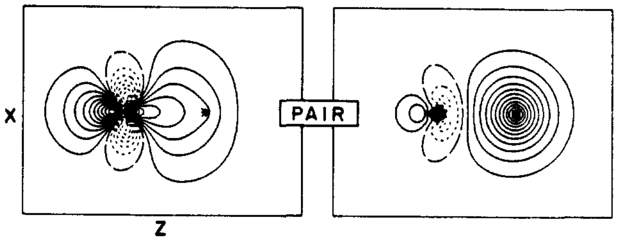
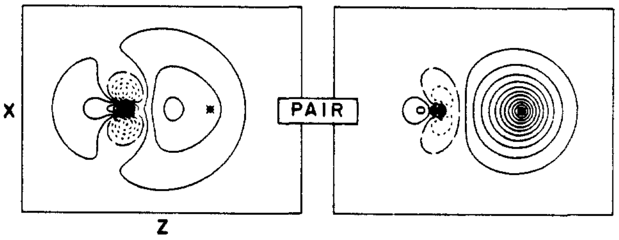
Table II. Spectroscopic Properties of MH^+

	ground state								bond energies (kcal/mol)				
		config of nonbonded electrons							theory			expt (D_{298})	
molecules	symmetry	δ	$\bar{\delta}$	π	$\bar{\pi}$	σ	bond distance R_e (Å)	vib freq[a] ω_e (cm^{-1})	D_e	D_0	D_{298}	*b*	*c*
CaH^+	$^1\Sigma^+$	0	0	0	0	0	1.940	1467	46.8	44.7	45.4		45.9 ± 2
ScH^+	$^2\Delta^\pm$	1	0	0	0	0	1.810	1631	57.5	55.2	56.1	54 ± 4	56.2 ± 2
TiH^+	$^3\Phi^\pm$	1	0	1	0	0	1.730	1696	56.4	54.0	54.9		56.0 ± 2
VH^+	$^4\Delta^\pm$	1	0	1	1	0	1.662	1749	46.1	43.6	44.5		48.2 ± 2
CrH^+	$^5\Sigma^+$	1	1	1	1	0	1.602	1818	26.9	24.3	25.2	35 ± 4	28.3 ± 2
MnH^+	$^6\Sigma^+$	1	1	1	1	1	1.702	1570	41.8	39.6	40.5	53 ± 3	52.3 ± 2
FeH^+	$^5\Delta^\pm$	2	1	1	1	1	1.653	1657	49.4	47.0	47.9	58 ± 5	54.9 ± 2
CoH^+	$^4\Phi^\pm$	2	1	2	1	1	1.606	1631	45.9	43.6	44.5	52 ± 4	48.4 ± 2
NiH^+	$^3\Delta^\pm$	2	1	2	2	1	1.561	1728	38.2	35.7	36.6	43 ± 2	39.0 ± 2
CuH^+	$^2\Sigma^+$	2	2	2	2	1	1.513	1793	23.5	20.9	21.8	30 ± 3	21.2 ± 2
ZnH^+	$^1\Sigma^+$	2	2	2	2	2	1.545 (1.514)[d]	1868 (1916)[d]	55.1	52.4	53.3		57.7[d] 57 ± 17[e] 49 ± 17[f]

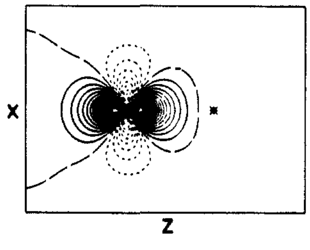
[a] From harmonic force constant at R_e. [b] Caltech (1978–1984); see ref 2, 3, 5, and 6. [c] Berkeley (1982–1984); see ref 4 and 7. [d] Experimental values; ref 14. [e] Reference 9. [f] Reference 8.



a) Cr^+– H σ BOND



b) Mn^+– H σ BOND



c) Mn^+– H d_{z^2} ORBITAL

Figure 1. Orbitals for $^5\Sigma^+$ CrH^+ and $^6\Sigma^+$ MnH^+ at the respective equilibrium geometries. (a) GVB orbitals for the Cr^+–H σ bond. The Cr^+ orbital is hybridized 40.6% s, 12.5% p, and 46.9% d. (b) GVB orbitals for the Mn^+–H σ bond. The Mn^+ orbital is hybridized 76.3% s, 12.5% p, and 11.2% d. (c) The MnH^+ singly-occupied d_{z^2} orbital. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au.

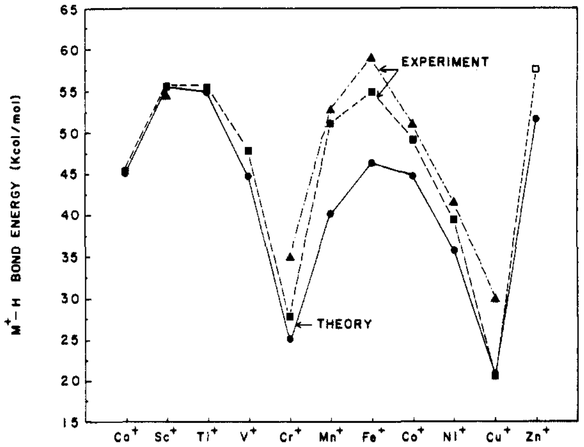


Figure 2. Comparison of experimental and theoretical bond dissociation energies: [$D_{298}(M^+–H)$] present work (closed circles); Beauchamp et al., ref 2, 3, 5, 6 (closed triangles); Armentrout et al., ref 4, 7 (closed squares); Herzberg, ref 14 (open square).

For ZnH^+, there is a $3d^{10}$ set of nonbonding orbitals so that there is essentially no d character in the bond (90.7% 4s, 8.9% 4p, and 0.4% 3d).

B. Bond Energies. The calculated bond energies show systematic fluctuations that are mirrored by the experimental results, as indicated in Figure 2 and Table II.

The simplest starting point for examining the bonding of H to M^+ is to consider M^+ in the $(4s)^1(3d)^{n-1}$ state and then to spin-pair the M^+ 4s and H 1s orbitals to form the σ bond. In some cases the ground state of M^+ is $(3d)^n$ so that the ΔE_{sd} promotion energy is required (weakening the bond). This causes particularly low bond energies for CrH^+ and CuH^+ since the $Cr^+(d^5)$ and $Cu^+(d^{10})$ states are particularly stable with respect to s^1d^4 and s^1d^9, respectively.

If the s^1d^{n-1} state were always the ground state and if the intrinsic M–H bond energy were the same for all bonds, there would be a gradual decrease in bond energy for Ca–Mn and a gradual increase from Fe to Zn because of changes in exchange terms. For example, in Mn^+, the high-spin ground state (s^1d^5) has a total exchange energy of

$$E^{ex} = -5K_{sd} - 10K_{dd}$$

but spin-pairing of the Mn 4s orbital with H 1s leads to an intraatomic exchange energy of

$$E^{ex} = -\tfrac{5}{2}K_{sd} - 10K_{dd}$$

This results in a weakening of the bond by

$$\Delta E^{ex} = \tfrac{5}{2}K_{sd} = 12.0 \text{ kcal}$$

On the other hand, for Sc^+ (s^1d^1) the loss in exchange energy upon bonding is only

$$\Delta E^{ex} = \tfrac{1}{2}K_{sd} = 3.6 \text{ kcal}$$

Making such adjustments for ΔE_{sd} and ΔE^{ex} leads to the predicted intrinsic bond energies, D_{sH}, in Table III. Excluding the three atoms with very strong preference for d^N (Cr^+, 36.7 kcal; Ni^+, 25.1 kcal; and Cu^+, 64.8 kcal), we find nearly constant D_{sH}: 59.7 (Sc), 60.6 (Ti), 60.5 (V), 52.5 (Mn), 57.7 (Fe), 61.9 (Co), and 53.3 (Zn). This leads to an average D_{sH} of $\bar{D}_{sH}$ = 58.0 kcal. For CaH^+ we obtain D_{sH} = 45.4 kcal/mol, indicating that the

Table III. Analysis of the Bond Energies for MH^+

	$D_{298}(M^+\text{-}H)$	ΔE_{exc}[a]	ΔK_{sd}[b]	D_{sH}[c]
CaH^+	45.4	0.0	0.0	45.4
ScH^+	56.1	0.0	3.6	59.7
TiH^+	54.9	0.0	5.7	60.6
VH^+	44.5	7.8	8.2	60.5
CrH^+	25.2	35.1	10.2	70.5
MnH^+	40.5	0.0	12.0	52.5
FeH^+	47.9	0.0	9.8	57.7
CoH^+	44.5	9.9	7.5	61.9
NiH^+	36.6	25.1	4.8	66.5
CuH^+	21.8	64.8	2.2	88.8
ZnH^+	53.3	0.0	0.0	53.3

[a] Experimental excitation energies for the $3d^{n-1}4s^1$ state obtained from ref 15 by using the average of the observed j states derived from each Russell–Saunders term. [b] Change in s–d exchange energy assuming a metal 4s-H 1s σ bond. [c] $D_{sH} = D_{298}(M^+\text{-}H) + \Delta E_{exc} + \Delta K_{sd}$.

bonding in Ca is significantly different from that in Sc, etc. [This probably arises from the high energy of the 3d orbital in Ca as compared with the transition metals.] For CrH^+ and NiH^+, the ΔE_{sd} corrections lead to somewhat larger bond energies (70.5 and 66.5 kcal, respectively), indicating that a higher fraction of d^n character may be involved in the bond. For CuH^+, the d^{10} to s^1d^9 excitation energy is quite large (64.8 kcal), and the estimated intrinsic D_{sH} is no doubt too large. Even with the apparent overestimate for Cr^+, Ni^+, and Cu^+, it is clear that the ΔE_{sd} and ΔE^{ex} corrections take the wildly fluctuating set of MH^+ bond energies into a rather smooth set of intrinsic bond energies. This validates the overall picture of bonding.

The theoretical bond energies are in particularly good agreement (average error 3.4 kcal) with the recent experimental results from the Armentrout group (Berkeley),[7] with differences (kcal/mol) of 0.4 (Ca), 0.1 (Sc), 1.1 (Ti), 3.7 (V), 3.1 (Cr), 11.8 (Mn), 7.0 (Fe), 3.9 (Co), 2.4 (Ni), –0.6 (Cu). For ZnH^+ the theoretical results lead to a bond energy 4.4 kcal weaker than experimental spectroscopic results.[14] The Armentrout experimental results are extracted from threshold extrapolations of studies on

$$M^+ + H_2 \rightarrow MH^+ + H$$

an extrapolation that is complicated by uncertainties in the amount of excited M^+ in the beam, in the form of the energy dependence of intensity near threshold, and in corrections for temperature broadening. Since the residual error in the theoretical calculations should be rather independent of metal, the theoretical results may help in designing more refined procedures of analyzing the experimental results.

C. Electronic Configuration. The electronic configurations for the *nonbonding* orbitals of MH^+ (see Table II) are easy to understand. The general pattern is that the number of electrons in σ nonbonding orbitals is minimized. Thus, all nonbonding electrons are π or δ for the sequence Sc–Cr, while all nonbonding electrons but one are π or δ for the sequence Mn–Cu. The explanation of the preferences between π and δ is as follows: The first electron goes into a δ orbital to minimize electron repulsion with the electrons in the σ bond. However, the second electron is π since two electrons in δ orbitals, both being in the *xy* plane, would have high electron repulsion. The third electron goes in the other π orbital since this puts all three nonbonding electrons in different planes (*xz*, *yz*, and *xy*). Thus, denoting the four orbitals as δ, $\bar{\delta}$, π, and $\bar{\pi}$, the sequence of configurations is δ, $\delta\pi$, $\delta\pi\bar{\pi}$, and $\delta\bar{\delta},\pi\bar{\pi}$ for Sc, Ti, V, and Cr, and the sequence for doubly-occupying orbitals is the same for Fe, Co, Ni, and Cu. For the $\delta\pi$ configuration there are two states, Φ and Π, but Φ is lower.

D. Spectroscopic Parameters. The trend in calculated bond distances is a gradual decrease from 1.94 Å (CaH^+) to 1.60 Å (CrH^+), a jump to 1.70 Å (MnH^+), and a gradual decrease to 1.51 Å (CuH^+), and then a jump to 1.55 Å (ZnH^+). This trend parallels the trend in atomic sizes where for Ca^+ to Cr^+ the atomic 4s orbital is *larger* than the MH^+ bond distance by 0.16, 0.21, 0.16, 0.14, and 0.13 Å, respectively (average 0.16). Similarly, for Mn^+ to Cu^+ the atomic 4s orbital is *smaller* than R_{MH^+} by 0.02, 0.03, 0.02, 0.01, and –0.01, respectively (average 0.01). For ZnH^+, the bond distance is 0.06 Å larger than the atomic 4s orbital. These trends correlate with the number of electrons in nonbonding $d\sigma$ orbitals. One electron in $d\sigma$ increases the bond distance by 0.15 Å; two increases it by another 0.07 Å.

There is an experimental value of R_e only for ZnH^+; it is 1.514 Å, which is 0.03 Å smaller than the calculated value.[14] The theoretical R_e should be slightly long (residual electron correlation would generally allow a contraction in various pair orbitals), and it is reasonable to assume about the same error for the other cases.

The origin in the trend for vibrational frequency is less clear. There is a big jump (1467 to 1631 cm^{-1}) for CaH^+ to ScH^+ and then a gradual increase to 1818 cm^{-1} for CrH^+. In this range there is a steady decrease in R_{MH^+}, and the *intrinsic* bond energy remains rather constant (the adiabatic bond energy decreases from Sc to Cr). There is a big drop to 1570 cm^{-1} for MnH^+ (corresponding to occupying a nonbonding $d\sigma$ orbital with a concomitant decrease of d character in the bond pair), even though the adiabatic bond energy increases dramatically. A reasonably steady increase is observed for the sequence Mn (1570 cm^{-1}) to Zn (1868 cm^{-1}). The experimental value[14] for ZnH^+ is 1916 cm^{-1}, about 5% larger than the calculated value. The theoretical value should be slightly too small (residual electron correlation would allow a deepening and shortening of the potential well leading to a higher force constant) and a similar error might be expected for other cases.

Summary

The GVB qualitative description of bonding allows reliable prediction of the symmetries of various MH^+ systems and provides a useful interpretation of the bond energies. In addition, the quantitative results are in excellent agreement with the experiment. These methods are quite practical for other MR^+ systems involving second- and third-row transition metals and should help in extracting reliable thresholds from experimental studies.

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Registry No. CaH^+, 23336-23-4; SCH^+, 83018-00-2; TiH^+, 83017-94-1; VH^+, 83018-01-3; CrH^+, 75641-98-4; MnH^+, 75641-96-2; FeH^+, 71899-96-2; CoH^+, 12378-09-5; NiH^+, 75181-25-8; CuH^+, 83017-95-2; ZnH^+, 41336-21-4.

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