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The low-lying states of the second-row transition metal hydrides (YH–CdH)

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Complete active space multiconfiguration self-consistent field (CAS-MCSCF) followed by full second-order configuration interaction calculations which included up to 713 000 configurations are carried out on the low-lying states of all second-row transition metal hydrides (YH–CdH). A large (6s5p5d 1f) valence Gaussian basis set together with relativistic effective core potentials which included the outer 4s²4p⁶4dⁿ5s² shells, were employed. The spectroscopic constants and potential energy curves of six electronic states of CdH are also obtained and compared with available experimental spectra. The ground states of YH, ZrH, NbH, MoH, TcH, RuH, RhH, PdH, AgH, and CdH were found to be ¹Σ⁺, ²Δ_{3/2}, 3(I), ⁶Σ⁺, ⁵Σ⁺, ⁴Σ_{1/2}[−], ³Δ, ²Σ⁺, ¹Σ⁺, and ²Σ⁺, respectively. For NbH, TcH, and RuH, ⁵Π, ⁷Σ⁺, and ⁴Φ states, respectively, were found to be close to the ground states. The ⁵Π₃ and ⁵Δ₃ states of NbH undergo avoided crossing. The spectroscopic constants (*r_e*, *μ_e*, *D_e*, *ω_e*, *T_e*) of the low-lying states of these hydrides are computed and compared with available data on YH, RhH, PdH, and AgH. The theoretical *r_e* and *ω_e* values are within 0.01 Å and 20 cm^{−1} of the experimental constants for these three hydrides.

I. INTRODUCTION

Theoretical and experimental studies of transition metal hydrides (TMH) have been the topic of several studies in recent years.^{1–29} TMHs are especially interesting since the bonding between the metal atom and H involves mixtures of 4dⁿ5s², 4dⁿ⁺¹5s¹, 4dⁿ5s¹5p and other configurations. The bonding in the second-row TMHs differ significantly from those of the first-row TMHs. Relativistic and spin–orbit effects are also known to be significant for the second and third TMHs compared to the first row.^{10–15}

Experimental studies on the second-row TMHs are restricted to the YH,^{19,25} RhH,^{27–29} PdH,^{16–18} and AgH.²⁴ These studies have, however, shed light only on a few states of the species. The YH molecule has recently been studied by Simard and co-workers²⁵ who also obtained the spectroscopic constants for the observed states.

Theoretical studies on second-row TMHs, include all-electron calculations by Lee and McLean on AgH,² ECP-CASSCF calculations on RuH by Krauss and Stevens,⁸ SCF/SDCI/MCPF calculations by Langhoff *et al.*⁹ on the low-lying states of YH–AgH as well as CASSCF/MRCI calculations from our laboratory on the spectroscopic constants of a large number of electronic states of YH,¹¹ ZrH,¹² MoH,¹³ TcH,¹⁴ RuH¹⁵, and PdH.¹⁰ The PdH molecule has also been studied by a few other workers⁶ but some of these calculations did not include relativistic effects and hence predicted bond lengths which were too long. The previous calculations from our lab are based on relativistic effective core potentials (RECPs) which retained the outer 4dⁿ5s² shells in the valence space replacing the rest of the electrons by RECPs. There is a question on the reliability and accuracy of the use of such RECPs although preliminary studies on

ZrH¹² revealed that the difference in the constants obtained using 4d²5s² (RECPs) versus 4s²4p⁶4d²5s² RECPs were mainly on *r_e*'s (~3% longer).

La John *et al.*³⁰ have generated RECPs for the second-row transition metal atoms which retain 4s²4p⁶4dⁿ5s² in the valence space. The reliability and accuracy of these RECPs have not been tested at all in molecular calculations up to now. Furthermore, it is important to gauge the accuracies of 4dⁿ5s² RECPs against 4s²4p⁶4dⁿ5s² RECPs in molecular calculations. To the contrary, Langhoff *et al.*⁹ have used the 4s²4p⁶4dⁿ5s² RECPs generated by Hay and Wadt³¹ for molecular calculations of the second-row TMHs. It would thus be important to compare the accuracies of the two RECPs.

Electronic states of the CdH molecule have not been theoretically studied up to now. For CdH we obtain both the spectroscopic constants for the ground state and potential energy curves for five excited states. There are some experimental studies on the electronic states of CdH^{23,24} which have revealed spectroscopic constants for some of the states we study in this investigation.

We employ a complete active space MCSCF (CAS-MCSCF) followed by full second-order CI (SOC) calculations including Davidson's corrections in conjunction with a large valence (6s6p5d 1f) Gaussian basis sets. It is shown that these calculations give the most accurate theoretical spectroscopic constants to date, *r_e* within 0.005–0.01 Å of experimental values, *ω_e* within 2–20 cm^{−1} of experimental values, dipole moments (*μ_e*) with an expected accuracy of 0.1–0.2 D. It is also shown that previous calculations⁹ yielded incorrect ground state for RuH and missed a very low-lying ⁵Π state of NbH which is a competitor for the ⁵Δ ground state of NbH. The *D_e*'s obtained in this study are much improved. The dipole moments obtained using the SCF/MCPF method are shown to be significantly larger

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($\sim 0.2\text{--}0.3$ D) compared to our CASSCF/SOCI values for YH, NbH, MoH and TcH, while a recent experimental study on YF²⁶ supports our μ_e value for YH. It is demonstrated that $4d^5 5s^2$ RECPs give very comparable spectroscopic constants for all TMHs heavier than RuH in the second row. For the lighter TMHs, the r_e 's obtained using $4d^5 5s^2$ ECPs tend to be $0.02\text{--}0.05$ Å longer, although ω_e 's and D_e 's are comparable. The T_e 's are also in general within 2000 cm^{-1} using either RECPs but only for TcH, it is shown that the use of $4d^5 5s^2$ RECPs favor the $^7\Sigma^+$ state as the ground state (T_e of $^5\Sigma^+ \sim 2600\text{ cm}^{-1}$) while the $4s^2 4p^6 4d^5 5s^2$ RECPs yield a $^5\Sigma^+$ ground state with a very low-lying $^7\Sigma^+$ excited state ($T_e \sim 1370\text{ cm}^{-1}$).

Section II describes our theoretical method of calculations. Section III, which is divided into ten subsections, discusses our CASSCF/SOCI-D spectroscopic constants of YH–CdH and compares them with other calculations and available data on YH, PdH, and AgH. For CdH, we include more extensive potential energy curves, spectroscopic constants, and comparisons with available experimental spectra of CdH.

II. METHOD OF CALCULATIONS

Relativistic effective core potentials (RECPs) generated by La John *et al.*³⁰ which retained the outer ($4s^2 4p^6 4d^5 5s^2$) or ($4s^2 4p^5 4d^{n+1} 5s^1$) valence shells of the second-row transition metal atoms are employed to investigate second-row TMHs. These authors have also optimized a valence ($5s 5p 4d$) Gaussian basis sets for these elements.³⁰ To this basis set we added a diffuse s function, a set of three diffuse p functions, and a set of six-component diffuse d functions. Note that we do not contract the basis functions corresponding to the $4s$ and $4p$ orbitals unlike the previous work.⁹ In terms of total energies, we find a large difference up to $2\text{--}3$ hartrees in contracting the $4s$ and $4p$ orbitals with generalized contractions. To reduce the possibility of basis set superposition errors and to preserve the nodal structure of the valence $5s$ orbital, we do not contract the functions which correspond to the $4s$ and $4p$ orbitals. We also add a set of ten-component $4f$ -type functions. The $4f$ exponent for each TMH was optimized at the complete active space MCSCF (CAS-MCSCF) level of theory near the CAS r_e of the ground state of TMH. In general we found a single set of optimized ten-component $4f$ functions superior to the three-Gaussian fit to a STO employed before.⁹ This is mainly because the $4f$ exponent in the present study is optimized for the molecule. Furthermore, for AgH, we add two sets of ten-component $4f$ functions. However, a critical comparison of the results of calculations with and without $4f$ functions indicated that $4f$ functions do not play a very significant role.^{11–15} The final basis set employed is thus of ($6s 6p 5d 1f$) or ($6s 6p 5d 2f$) quality. For the hydrogen atom, we use van Duijneveldt's ($7s 1p/4s 1p$) basis set. The hydrogen basis set is thus better than triple zeta + polarization quality. The basis sets of La John *et al.* were found to be satisfactory for all TMHs except PdH for which in the asymptotic limit the $\text{Pd}(^3D)$ state is favored over $\text{Pd}(^1S)$. Hence we correct the D_e obtained for PdH using the $\text{Pd}(^3D)\text{--Pd}(^1S)$ separation of 0.72 eV obtained before.¹⁰

We use the complete active space MCSCF (CAS-MCSCF) method to optimize orbitals for configuration interaction (CI) calculations. In the CAS-MCSCF method, the active (valence) electrons are distributed in all possible ways among a chosen set of most important orbitals referred to as the active orbitals. To maintain consistency in the treatment, we uniformly kept the outer $4d^5 5s^2$ ($4d^{n+1} 5s^1$) valence shells of the TM atom and the H $1s^1$ shell as active. Excitations from the semicore $4s^2 4p^6$ orbitals were not allowed, although the coefficients of these orbitals were allowed to change as a function of geometry. The active space in the CASSCF was uniformly kept as those orbitals which correlate into the metal $4d$, $5s$, and H ($1s$) orbitals at infinite separation for all TMHs. For CdH since the excited states arise from $4d^{10} 5s 5p$ and other Rydberg configurations, two sets of CAS-MCSCF calculations were carried out. The first set for the $^2\Sigma^+$ ground state is in accordance with the procedure described for other TMHs. The second set included the $5s$ and $5p$ orbitals of the Cd atom in the active space. In the latter method of calculations, excitations from the $4d^{10}$ shells were not allowed at the CAS-MCSCF stage.

Higher-order electron correlation effects were included using the full second-order configuration interaction (SOCi) method after the CAS-MCSCF. The SOCi calculations include (i) all configurations in the CAS-MCSCF, (ii) configurations generated by distributing $n + 2$ electrons (recall, the valence shell is $4d^5 5s^2$) in the active space and one electron in the orthogonal external space in all possible ways, (iii) $n + 1$ electrons in the active space and two electrons in the external space in all possible ways.

We also obtain the effect of unlinked quadruple clusters not included in the full SOCi method using a modified version of the Davidson formula shown below for the SOCi method:

$$\Delta E^c = (E^{\text{SOCi}} - E^{\text{REF}}) \left(1 - \sum_{i=1}^{n_c} C_i^2 \right),$$

where E^{SOCi} is the SOCi energy, E^{REF} is the energy of the CAS-MCSCF configurations in the SOCi expansion obtained by setting the coefficients of non-CAS-MCSCF configurations to zero, n_c is the number of CASSCF configurations, and C_i is the coefficient of the i th CASSCF configuration in the SOCi expansion. Consequently, the present study on TMHs includes all important dynamic electron correlation effects.

The potential energy curves of the ground state and five excited electronic states of CdH are obtained using a method which we denote as d-FOCI. The d-FOCI was made using a $3e$ CASSCF which retained both the $5s$ and $5p$ orbitals of Cd in the active space. In the d-FOCI calculation of CdH, we include configurations generated by distributing (i) three active electrons in the internal space all possible ways, (ii) two electrons in the ($5s\text{--}5p$) active space and one electron in the external space in all possible ways, (iii) nine d electrons and one electron in the external space in all possible ways. Hence the d-FOCI includes important d , s and p excitations into the external space for CdH.

The effect of spin-orbit coupling has already been studied on most of the second-row TMHs except CdH using the

RCI method. In the present study, the spin-orbit effects of CdH are also included using the RCI method. Consequently, the present study is the most accurate theoretical study of the second row TMHs. We expect the bond lengths to be in general accurate to 0.005 Å, ω_e 's within 5% of the experimental values, μ_e 's within ± 0.1 D and D_e 's within 0.1–0.2 eV of experimental values. The only exception appears to be AgH for which ($4s^2 4p^6$) core–valence correlation effects seem to be important and hence our SOCI r_e is 0.01 Å larger than the experimental value.

We consider competing low-lying electronic states as candidates for the ground state. For YH, an excited $^1\Pi$ state was also studied mainly to gauge the accuracies of previously reported T_e 's. We consider $^2\Delta$ and $^4\Phi$ states of ZrH, two very-low lying $^5\Delta$ and $^5\Pi$ states of NbH, $^6\Sigma^+$ state of MoH, $^5\Sigma^+$ and $^7\Sigma^+$ states of TcH, $^4\Sigma^-$ and $^4\Phi$ states of RuH, $^3\Delta$ state of RhH, $^2\Sigma^+$ state of PdH, and the $^1\Sigma^+$ ground state of AgH. Since CdH has not been theoretically studied at all, the potential energy curves of six electronic states of CdH are obtained. In addition, the spectroscopic constants of these states are obtained and compared with available experimental data. The RCI calculations of CdH were made using $^3\Sigma^-$ orbitals of CdH[−] so that the $5p$ orbital is occupied and ($5p_x, 5p_y$) degeneracy is maintained.

The present SOCI calculations included up to 713 000 configurations while the CAS-MCSCF calculations included up to 120 configurations. All CAS-MCSCF/SOCI calculations were made using the author's³² modified version of ALCHEMY II codes.³³ The relativistic CI (RCI) calculations of CdH were made using the general method of Gaussian-RCI for polyatomics described in Ref. 34. The spin-orbit integrals in gaussian basis sets were obtained using Pitzer's codes.³⁵

III. RESULTS AND DISCUSSION

A. YH

Table I shows the spectroscopic constants of the $X^1\Sigma^+$ and the lowest $^1\Pi$ excited state of YH obtained using the full second-order CI method and Davidson's correction. Also shown in that table are the corresponding SCF/MCPF values obtained by Langhoff *et al.*⁹ using the Hay–Wadt³¹ ($4s^2 4p^6 4d^1 5s^2$) RECPs for yttrium. The SCF/MCPF method yields a r_e 0.007 Å longer than the CAS/SOCI value for the $X^1\Sigma^+$ ground state. The vibrational frequencies obtained using the two procedures are very comparable. The D_e obtained including Davidson's correction is 3.01 eV com-

pared to a SCF/MCPF value of 2.95 eV for the $X^1\Sigma^+$ ground state.

The dipole moment obtained using the CAS/SOCI method is ~ 0.3 D smaller than the SCF/MCPF method. The dipole moment of YF has been recently measured experimentally by Simard, Steimle, and co-workers²⁶ as 1.825 ± 0.007 D. We expect the dipole moment of YH to be much smaller than the μ_e of YF. Consequently, the μ_e value obtained using the SCF/MCPF procedure is 0.3 D too high. The spectroscopic constants predicted by the SCF/MCPF method for the $^1\Pi$ state are in much better agreement with the exception of the T_e value. The SCF/MCPF T_e of the $^1\Pi$ state is roughly 1000 cm^{-1} higher.

A comparison of the spectroscopic constants obtained by the author and Wang¹¹ using ($4d^1 5s^2$) RECPs in conjunction with smaller ($3s 3p 3d 1f$) basis set reveals that the ω_e values, T_e and D_e are in very good agreement with the corresponding values obtained using ($4s^2 4p^6 4d^1 5s^2$) RECPs and a ($6s 6p 5d 1f$) basis set. For example the ω_e and D_e value of the $X^1\Sigma^+$ state obtained¹¹ using the ($4d^1 5s^2$) RECPs are 1510 cm^{-1} and 3.05 eV in excellent agreement with the 1522 and 3.01 eV obtained in the present study. Similarly the T_e and ω_e values of the $^1\Pi$ state using ($4d^1 5s^2$) RECPs are $12\,685$ and 1380 cm^{-1} compared to $11\,788$ and 1367 cm^{-1} , respectively, obtained using ($4s^2 4p^6 4d^1 5s^2$) RECPs of La John *et al.*³⁰ Hence the main difference is in the r_e values. The $3e$ RECPs yielded r_e 's of 1.87 and 1.94 Å for the $X^1\Sigma^+$ and $^1\Pi$ states, respectively, compared to 1.95 and 2.01 Å obtained using the $11e$ RECPs. Consequently for YH, $3e$ RECPs yield r_e 's approximately 0.07 – 0.08 Å shorter than their true values. Since the r_e changes are uniform for all electronic states, it is evident that the experimental trend can be predicted using $3e$ RECPs. However, $3e$ RECPs are not expected to be reasonable for very ionic species such as YO, YF, etc. or for clusters such as Y_2 and Y_3 . For such species it is necessary to use $11e$ RECPs since the nodeless $5s$ orbital yields bond lengths which are unreasonably small for such species.

The D_e obtained using the CAS/SOCI (D) needs to be corrected for spin-orbit effects. The $^1\Sigma_0^+$ ground state is lowered by only 11 cm^{-1} due to spin-orbit coupling near its r_e . However, the YH 0^+ state dissociates into $Y(^2D_{3/2}) + H(^2S_{1/2})$. The $Y(^2D_{3/2})$ state is stabilized by 300 cm^{-1} with respect to $Y(^2D)$. Consequently, the effect of spin-orbit coupling will reduce the D_e of YH to 2.96 eV. If

TABLE I. Spectroscopic constants of the $^1\Sigma^+$ and $^1\Pi$ electronic states of YH.^a

State	r_e (Å)		ω_e (cm^{-1})		μ_e (D)		T_e (cm^{-1})		D_e (eV)	
	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF
$^1\Sigma^+$	1.954	1.961	1522	1559	1.28	1.535	0	0	2.93 (3.00)	2.95
$^1\Pi$	2.015 (2.014)	2.024	1367 (1375)	1364	3.2	3.17	11 788 (11 722)	10 889		

^aNumbers in parentheses include Davidson's correction. In all subsequent tables positive polarity of dipole moment means M^+H^- polarity. MCPF values from Ref. 9.

zero-point correction is applied based on our ω_e , the experimental D_0^0 (YH) is predicted as 2.77 ± 0.1 eV. The error bar is for the effect of higher-order correlations and basis set improvements.

B. ZrH

Table II shows the spectroscopic constants of $^2\Delta$, $^4\Phi$ electronic states of ZrH and their spin-orbit components obtained using the CAS/SOCI/RCI method. As seen from Table II, the ground state of ZrH is the $^2\Delta_{3/2}$ state at the highest level of theory in agreement with previous prediction.¹² In the absence of spin-orbit effects, the $^2\Delta$ state is the ground state in accord with Langhoff *et al.*'s SCF/MCPHF study.⁹ The r_e values of both the $^2\Delta$ and $^4\Phi$ states obtained in the present study using the SOCI method are 0.05 and 0.005 Å, respectively, shorter than the r_e 's obtained using the SCF/MCPHF method.¹² This is primarily because the weight of the leading configuration in the $^2\Delta$ state is less than 75% while the weight of the $^4\Phi$ state is higher than 92%. Consequently, SCF/MCPHF method is expected to be inferior to the CAS-MCSCF/SOCI method for electronic states whose leading configuration(s) contain weights < 85%. Consequently, the claimed accuracy of 0.02 Å⁹ is not valid for ZrH.

The vibrational frequency (ω_e) of the $^2\Delta$ state predicted by the SCF/MCPHF method⁹ is in poor agreement with a more accurate CAS/SOCI method mainly because of the need for a MCSCF/MRCI treatment for the $^2\Delta$ state while the $^4\Phi$ state is satisfactorily represented by a single configuration. Hence the ω_e of the $^4\Phi$ state of ZrH obtained using both methods are in excellent agreement while the SCF/MCPHF method gives substantially different ω_e for the $^2\Delta$ state. The agreement in the μ_e of the $^2\Delta$ state of ZrH in Table II should therefore be considered fortuitous due to the cancellation of effect of correlation on μ_e and the effect of longer r_e obtained in Ref. 9.

As seen from Table II, the $^2\Delta_{3/2}$ – $^2\Delta_{5/2}$ and $^4\Phi_{3/2}$ – $^4\Phi_{5/2}$ spin-orbit separations are 546 and 970 cm^{−1}, respectively. Therefore, spin-orbit effects are quite significant and cannot be neglected for ZrH. The previous SCF/MCPHF study⁹ neglected the effect of spin-orbit coupling. The RECPs of La John *et al.*³⁰ are thus superior to the Hay-Wadt RECPs³¹ in this aspect, although the two RECPs give comparable spectroscopic constants in the absence of spin-orbit coupling. We note that the difference in the r_e and ω_e for the $^2\Delta$ state between the SCF/MCPHF and CAS/SOCI methods is because of the inadequacy of the former method to represent electronic states for which leading configuration makes less than 85%–90% contribution than due to any defect in the Hay-Wadt ECPs.³¹ This is evidently established by a comparison of the properties of the $^4\Phi$ state.

C. NbH

Table III shows the spectroscopic constants of the $^5\Delta$ and $^5\Pi$ electronic states of NbH and the T_e values of the spin-orbit components. There are no experimental data on NbH for comparison. We include the previous SCF/MCPHF values of the $^5\Delta$ state for comparison.

As seen from Table III, NbH has two states within 700 cm^{−1} of each other in the absence of spin-orbit coupling. The energy separation reduces to 600 cm^{−1} when Davidson's correction is included. The previous SCF/MCPHF⁹ study did not consider the $^5\Pi$ state of NbH. It is, however, a competitor for the ground state with $^5\Delta$ as seen from Table III. The r_e obtained in this study for the $^5\Delta$ state in the absence of spin-orbit coupling is 0.004 Å shorter than the previous SCF/MCPHF value.⁹ The CASSCF/SOCI ω_e (1725 cm^{−1}), however, differs significantly from the SCF/MCPHF value of 1583 cm^{−1}. Similarly our μ_e of the $^5\Delta$ state is 0.2 D smaller than the SCF/MCPHF value, a trend consistent with our results on YH. The D_e of the $^5\Delta$ state is also quite comparable in the absence of spin-orbit coupling.

TABLE II. Spectroscopic constants of the $^2\Delta$ and $^4\Phi$ states of ZrH.^a

State	r_e (Å)		ω_e (cm ^{−1})		μ_e (D)		T_e (cm ^{−1})		D_e (eV)	
	SOCI	MCPHF	SOCI	MCPHF	SOCI	MCPHF	SOCI	MCPHF	SOCI	MCPHF
$^2\Delta(3/2)$	1.811 (1.816)	...	1815 (1965)	0	0		
$^2\Delta$	1.811 (1.816)	1.857	1784 (1934)	1483	1.24	1.23	292	0	2.47 (2.44)	2.45
$^2\Delta(5/2)$	1.811 (1.816)	...	1817 (1967)	546	...		
$^4\Phi(3/2)$	1.897 (1.895)	...	1569 (1557)	1056 (1321)	...		
$^4\Phi(5/2)$	1.897 (1.895)	...	1570 (1558)	1348 (1613)	...		
$^4\Phi$	1.897 (1.895)	1.902	1570 (1558)	1532	2.13	2.42	1497 (1762)	565		
$^4\Phi_{7/2}$	1.897 (1.895)	...	1571 (1559)	1634 (1899)	...		
$^4\Phi_{9/2}$	1.897 (1.895)	...	1571 (1559)	1925 (2190)	...		

^aNumbers in parentheses include Davidson's correction. MCPHF values from Ref. 9.

TABLE III. Spectroscopic constants and spin-orbit splittings of NbH.^a

State	r_e (Å)		ω_e (cm ⁻¹)		T_e (cm ⁻¹)		μ_e (D)		D_e (eV)	
	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF
⁵ Δ	1.788 (1.787)	1.791	1725	1583	0	0	2.29	2.45	2.67 (2.70)	2.60
⁵ Π	1.810	...	1709	...	712 (607)	...	2.68	...	2.58	...
					Spin-orbit state	T_e (cm ⁻¹)				
					3(I)	0				
					⁵ Π ₂	341				
					⁵ Δ _{0+,0}	405				
					⁵ Δ ₁	439				
					3(II)	558				
					⁵ Δ ₂	687				
					⁵ Δ ₄	1190				

^a Numbers in parentheses include Davidson's correction. The ⁵Δ₃ and ⁵Π₃ states undergo avoided crossing. Hence they are designated 3(I) and 3(II). MCPF values from Ref. 9. Spin-orbit splittings from Ref. 39.

As seen from Table III, spin-orbit splittings are quite significant for both the ⁵Δ and ⁵Π states of NbH. The ⁵Δ₀₊–⁵Δ₄ separation is 834 cm⁻¹. The Nb atom has a ⁶D_{1/2} ground state.³⁶ From the energy separations of the spin-orbit states of the Nb atom in Ref. 36, we estimate the ⁶D_{1/2}–⁶D splitting to be 634 cm⁻¹. Since the ⁵Δ₀₊–⁵Δ separation of NbH is 390 cm⁻¹, the D_e of NbH will be reduced by 244 cm⁻¹. Consequently, we predict the D_e (NbH) including spin-orbit effects as 2.64 ± 0.2 eV. The error bar allows for changes in the D_e for extension of basis sets, core-valence correlations, etc.

The substantial difference in the dipole moment of the ⁵Δ and ⁵Π states (0.44 D) will certainly facilitate the assignment of the ground state of NbH if the dipole moment of NbH can be measured.

The ⁵Δ₃ state of NbH is destabilized with respect to ⁵Δ while the ⁵Π₃ state is lowered with respect to ⁵Π. Consequently, the $\Omega = 3$ components of the two states undergo avoided crossing. This brings down the 3(I) state (⁵Π₃ + ⁵Δ₃) with respect to ⁵Π, making the 3(I) state as the lowest state at the RCI level. At short distances ($r = 3.0$ a.u.), the 3(I) state becomes 43% ⁵Δ₃ and 21% ⁵Π₃. At $r = 3.5$ a.u., the 3(I) state becomes 43% ⁵Δ₃ and 42% ⁵Π₃. Therefore we designate the two $\Omega = 3$ states as 3(I) and 3(II). Hence our description of NbH including spin-orbit coupling differs significantly from the previous study⁹

which neglected spin-orbit effects. We conclude that NbH has two nearly degenerate states of (⁵Π + ⁵Δ)₃ and ⁵Δ₀₊ symmetries.

D. MoH

Table IV shows the ground state constants of MoH. The ground state of MoH unlike NbH, is unequivocally established as the ⁶Σ⁺ state. The spin-orbit effects are also negligible for the ground state since it is a Σ⁺ state and therefore only through second-order spin-orbit contamination there could be any contribution by the spin-orbit operator. The CASSCF/SOCI r_e value is thus in excellent agreement with the SCF/MCPF value.⁹ The Davidson-corrected SOCI r_e is only 0.001 Å shorter than the SCF/MCPF method. The ω_e value predicted by the SCF/MCPF method is, however, 60 cm⁻¹ smaller. The SOCI dipole moment is 0.2 D smaller than the SCF/MCPF value. That is primarily because a single configuration SCF method used in the latter procedure yields too ionic bonding which is subsequently corrected but not adequately by the MCPF procedure. The Davidson-corrected D_e value is 0.11 eV larger than the SCF/MCPF method. Since spin-orbit coupling is negligible for both near the well and at the dissociation limit, our Davidson-corrected SOCI value of 2.30 eV for MoH could be at most 0.1 eV in error. Consequently, we establish the D_e (MoH) = 2.3 ± 0.1 eV. There is an experimental D (Mo–

TABLE IV. Spectroscopic constants of MoH.^a

State	R_e (Å)		ω_e (cm ⁻¹)		μ_e (D)		D_e (eV)		Expt.
	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	
⁶ Σ ⁺	1.747 (1.745)	1.746	1701 (1714)	1642	2.84	3.03	2.25 (2.30)	2.19	2.3

^a Numbers in parentheses include Davidson's correction. The MCPF values from Ref. 9. Experimental D (MoH) at 300 K is from Ref. 27.

H) = 2.3 ± 0.2 eV at 300 K listed by Armentrout and Beauchamp.²⁷ This value supports our D_e (MOH) = 2.3 eV since the zero-point corrected experimental D_e is 2.4 eV. Therefore, the MCPF method underestimates the D_e of MoH by 0.2 eV.

E. TcH

TcH is an interesting candidate for theoretical studies since different levels of theory yield different ground states for TcH. A previous CASSCF/MRSDCI study¹⁴ which used $4d^5 5s^2$ RECPs yielded a $^7\Sigma^+$ ground state and a very low-lying $^5\Sigma^+$ excited state at 2619 cm^{-1} . Note that for the $^7\Sigma^+$ state of TcH the CASSCF method is no more than a SCF since all configurations in the CASSCF are Brillouin singles with respect to the leading configuration and thus are annihilated through the operation of Brillouin's theorem. However, this is not the case for the low-spin $^5\Sigma^+$ state. Therefore, our earlier CASSCF/MRSDCI study for the TcH $^7\Sigma^+$ is tantamount to a SCF/SDCI procedure although this is not the case for the $^5\Sigma^+$ state. Nevertheless, we note that the $(4d^5 5s^2)$ RECPs in conjunction with $(4s3p4d\ 1f)$ basis yielded a $^7\Sigma^+$ ground state in accord with Langhoff *et al.*'s SCF/SDCI method⁹ which employed the Hay-Wadt $(4s^2 4p^6 5d^5 5s^2)$ RECPs. However, they obtain a $^5\Sigma^+$ state as the ground state using the SCF/MCPF method and claim that they are almost sure that at the highest level of theory, $^5\Sigma^+$ is the ground state.

As seen from Table V, the $15e$ La John *et al.*³⁰ RECPs and a $(6s6p5d\ 1f)$ basis set in conjunction with a CASSCF/SOCI-D procedure yields a $^5\Sigma^+$ ground state. The $^7\Sigma^+$ state is, however, only 1320 cm^{-1} above the $^5\Sigma^+$ ground state in the absence of spin-orbit interaction. The Davidson correction (almost 883 cm^{-1}) stabilizes the $^5\Sigma^+$ state further. However, the situation is complicated by the fact that the $^7\Sigma^+(7)$ spin-orbit state is stabilized by $\sim 610\text{ cm}^{-1}$ when spin-orbit coupling is introduced while the $^5\Sigma^+$ state is stabilized by only $\sim 80\text{ cm}^{-1}$. Consequently in the absence of the Davidson correction, the $^7\Sigma^+(7)-^5\Sigma^+(5)$ separation is only 790 cm^{-1} . Consequently, we conclude that the ground state of TcH is probably $^5\Sigma^+(2)$ but by no means is this definite contrary to the claim of Langhoff *et al.*⁹ who neglected spin-orbit effects.

The r_e of the $^7\Sigma^+$ state obtained using the SCF/SOCI-

D method is 0.01 \AA shorter than the MCPF value while the r_e of the $^5\Sigma^+$ state is $\sim 0.03\text{ \AA}$ (0.04 \AA when Davidson's correction is incorporated) longer than the SCF/MCPF method. The bond length increases as more electron correlation effects are included for the $^5\Sigma^+$ state. This is consistent with the SCF/SDCI bond length of 1.661 \AA and a SCF/MCPF bond length of 1.671 \AA obtained by Langhoff *et al.*⁹

The dipole moment for the $^5\Sigma^+$ state obtained using the CASSCF/SOCI method is 0.22 D larger than the SCF/MCPF value consistent with the bond length trend. However, the μ_e 's of the $^7\Sigma^+$ state are almost identical using either procedures since the r_e 's are more comparable. This is primarily because electron correlation effects are significant for the $^5\Sigma^+$ state.

The Davidson-corrected SOCI D_e of the $^5\Sigma^+$ state of TcH is 2.17 eV compared to the SCF/MCPF value of 1.95 eV .⁹ Hence the MCPF method underestimates the D_e (TcH) by 0.22 eV . Since spin-orbit effects are comparable for TcH near the well and dissociation limit, we predict D_0^0 (TcH) = $1.97 \pm 0.1\text{ eV}$.

F. RuH

Spectroscopic constants of the lowest-lying $^4\Sigma^-$ and $^4\Phi$ states and their spin-orbit states of RuH are shown in Table VI. As seen from Table VI, the ground state of RuH is a $^4\Sigma^-(1/2)$ state at the highest level of theory. The CASSCF/SOCI method using $(4s^2 4p^6 4d^6 5s^2)$ RECPs give the same ground state as the $(4d^6 5s^2)$ RECPs for Ru in agreement with the ground state predicted before.¹⁵ A single configuration SCF/MCPF method, however, yields a $^4\Phi$ ground state. The $^4\Sigma^-$ state of RuH cannot be adequately represented by a single configuration SCF approximation. Krauss and Stevens⁸ obtained the $^4\Phi$ state as the lowest state of RuH at the CASSCF level but they did not study all possible low-lying states. Their aim in studying RuH was to calibrate the RECPs of Ru for their calculations on RuO. Also, the CASSCF method is merely a zeroth-order description. However, Langhoff *et al.*⁹ studied the $^4\Delta$ and $^6\Delta$ excited states of RuH, but they find $^4\Phi$ to be the lowest. It appears that these authors did not consider the $^4\Sigma^-$ state but in an SCF approximation to obtain orbitals for a SDCI or MCPF method the $^4\Sigma^-$ state of RuH is not well represented. Fur-

TABLE V. Spectroscopic constants of TcH.^a

State	R_e (Å)		ω_e (cm ⁻¹)		μ_e (D)		T_e (cm ⁻¹)		D_e (eV)	
	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF
$^5\Sigma^+(5)$	1.704 (1.713)	...	1841 (1828)	0
$^5\Sigma^+$	1.704 (1.713)	1.671	1841 (1828)	1797	2.37	2.15	80	0	2.08 (2.17)	1.95
$^7\Sigma^+(7)$	1.824 (1.824)	...	1580	793
$^7\Sigma^+$	1.824 (1.824)	1.833	1580	1531	0.77	0.75	1400	1130	1.89 (1.87)	1.81

^a Numbers in parentheses include Davidson's correction. MCPF values from Ref. 9.

TABLE VI. Spectroscopic constants of two low-lying states of RuH.^a

State	R_e (Å)		ω_e (cm ⁻¹)		μ_e (D)		T_e (cm ⁻¹)		D_e (eV)		Expt
	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	
⁴ Σ ⁻ (1/2)	1.613(1.609)	...	1911	0	2.55
⁴ Σ ⁻	1.613(1.609)	...	1911 (1934)	...	2.4	...	87	...	2.61	...	
⁴ Φ (9/2)	1.641(1.636)	...	1830	256	2.34
⁴ Φ	1.641(1.636)	1.647	1830 (1847)	1801	2.62	2.70	1453 (1486)	0	2.44	2.34	

^aNumbers in parentheses include Davidson's correction. In the absence of spin-orbit interaction the SCF/MCPF method predicts ⁴Φ as the ground state (Ref. 9). The experimental $D(\text{Ru-H}) = 2.4 \pm 0.2$ eV at 300 K from Ref. 27 was corrected for the zero-point correction.

thermore, there is mixing of $\sigma\delta^2$ (89%) and $\sigma\pi^2$ configurations in the ⁴Σ⁻ ground state of RuH. Consequently, our more accurate CAS/SCF followed by full second-order CI calculations which include up to 640 000 configurations are in disagreement with the SCF/MCPF study of Langhoff *et al.* for RuH in the absence of spin-orbit coupling. The ⁴Φ state is found to be 1400 cm⁻¹ above the ⁴Σ⁻ ground state when Davidson's correction was included to the second-order CI. The CAS MCSCF/SOCI r_e of the ⁴Φ state (1.641 Å) is, however, in good agreement (0.006 Å shorter) with the SCF/MCPF value. The ω_e and μ_e are also in good accord for the ⁴Φ state. Since Langhoff *et al.*⁹ obtain ⁴Φ state as the lowest for RuH, their calculated D_e of 2.34 eV is also considerably lower than our CASSCF/SOCI D_e of the ⁴Σ⁻ state (2.61 eV). The experimental $D(\text{Ru-H}) = 2.4 \pm 0.2$ eV²⁷ at 300 K when corrected for zero-point correction yields a value of 2.55 ± 0.2 eV in excellent agreement with our value and thus supporting our CAS/SOCI study.

As seen from Table VI, the spin-orbit effects are also quite significant for RuH. The ⁴Σ⁻ (3/2)–⁴Σ⁻ (1/2) spin-orbit splitting for RuH is calculated as 87 cm⁻¹ while the ⁴Φ (9/2)–⁴Φ separation is 1195 cm⁻¹. Consequently, in the presence of spin-orbit coupling the ⁴Σ⁻ (1/2)–⁴Φ (9/2) splitting is only 256 cm⁻¹. Thus our description of RuH differs significantly from that of Langhoff *et al.*⁹ We conclude that both ⁴Σ⁻ (1/2) and ⁴Φ (9/2) states are candidates for the ground state of RuH but ⁴Σ⁻ (1/2) is lower of the two at the highest level of theory.

G. RhH

Table VII shows the spectroscopic constants of the ³Δ ground state of RhH. Both CASSCF/SOCI and SCF/MCPF methods predict the same ground state for RhH. The CASSCF/SOCI r_e is within 0.001 Å of the

SCF/MCPF method.⁹ The ω_e 's are also within the accuracies of the two procedure. The μ_e of the ground state of RhH is in excellent agreement. The primary reason for the good agreement between the CASSCF/SOCI and MCPF methods for RhH is because the ³Δ ground state orbitals are well described by a SCF treatment since the leading configuration dominates (> 91%) near the well.

The SOCI calculations of RhH included 713 000 CSFs. The D_e obtained this way including Davidson's corrections is 2.97 eV. This value is 0.16 eV higher than the SCF/MCPF value of 2.81 eV.

Tolbert and Beauchamp²⁸ have measured accurately the $D(\text{RhH})$ as 2.56 ± 0.22 eV. Note that this value does not include the zero-point correction. Hence we corrected this D using our calculated ω_e for the zero-point correction. As seen from Table VII both our results and the MCPF results seem to suggest that the zero-point corrected experimental value is 0.1–0.2 eV lower than the true value but Tolbert and Beauchamp give an error bar of ± 0.2 eV.

Illas *et al.*³⁸ have studied RhH using pseudopotential SCF/CIPSI method. They obtain the same ground state as ours and Langhoff *et al.* But the D_e (2.55 eV) of RhH obtained by these authors is 0.25 eV lower than Langhoff *et al.* and 0.3 eV lower than ours. Illas *et al.* compare their values with an experimental value without zero-point correction. Therefore their claimed agreement with experiment is not completely correct since the experimental value they use in comparison is the D value at 300 K and does not include zero-point energy. Therefore, we conclude that the CI-PSI method underestimates the electron correlation effects. This also explains the differences between our previous results³⁷ and Illas *et al.* results on Rh₂.

For RhH the use of $(4d^7 5s^2) 9e$ RECPs provide results in very good agreement with $(4s^2 4p^6 4d^7 5s^2)$ ECPs. For example, CASSCF/FOCI method with a significantly smaller

TABLE VII. Spectroscopic constants of the ground state of RhH.^a

State	R_e (Å)		ω_e (cm ⁻¹)		μ_e (D)		D_e (eV)		Expt.
	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	SOCI	MCPF	
³ Δ	1.576	1.575	1971	2057	2.28	2.24	2.85 (2.97)	2.81	2.70

^aThe experimental $D(\text{Rh-H})$ at 300 K from Ref. 27 has an uncertainty of ± 0.2 eV was corrected for the zero-point energy. The MCPF values from Ref. 9.

TABLE VIII. Spectroscopic constants of PdH.^a

State	R_e (Å)			ω_e (cm ⁻¹)			μ_e (D)		D_e (eV)		
	SOCI	MCPF	Expt.	SOCI	MCPF		SOCI	MCPF	SOCI	MCPF	Expt.
$^2\Sigma^+$	1.545	1.54	1.534	2081	1958		2.13	2.33	2.34 (2.41)	2.22	2.4

^a Experiment $D(\text{Pd-H})$ at 300 K has an uncertainty of ± 0.3 eV and was corrected for zero-point correction. The MCPF values from Ref. 9.

basis set and $(4d^7 5s^2)$ 9e ECPs gave $r_e = 1.54$ Å and $\omega_e = 2027$ cm⁻¹ and $D_e = 2.54$ eV. for RhH. Consequently, Rh is the turning point for the second row for which $(4s^2 4p^6 4d^7 5s^2)$ and $(4d^7 5s^2)$ ECPs give almost the same results except for a difference of 0.01–0.03 Å in r_e . This also corroborates with our previous study on Rh_2 (Ref. 37) for which the r_e 's of low-lying states were reasonable.

H. PdH

Table VIII shows the spectroscopic constants of PdH. For PdH there is an experimental r_e of 1.534 Å. Our CASSCF/SOCI method yields a bond length for the $^2\Sigma^+$ ground state within 0.005 Å of the experimental value of PdH. The SCF/MCPF procedure yields 0.01 Å longer bond length. There are other theoretical studies on PdH such as the one by Bagus and Björkman.⁶ The calculations of Bagus and Björkman⁶ do not include relativistic effects and thus yield much longer bond lengths. The spin-orbit coupling effect was shown to be very important for the excited state of PdH in a previous study.¹⁰ The excited $^2\Pi_{3/2}$ and $^2\Delta_{3/2}$ states for PdH undergo avoided crossing. Therefore it is not justified to neglect the spin-orbit effects for the excited states of PdH but for the $^2\Sigma^+$ ground state, the effect of spin-orbit coupling is small.

The D_e of PdH has been the topic of a few studies. An approximate experimental D_e of PdH was obtained by Malmberg *et al.*¹⁸ using the formula

$$D_e = \omega_e^2 / (4\omega_e x_e).$$

The value deduced this way (3.3 eV) is, however, too large as seen from Table VIII. The $D(\text{Pd-H})$ listed by Armentrout and Beauchamp at 300 K is 2.42 ± 0.26 eV and supports both our CAS/SOCI value corrected for the asymptotic separation and MCPF⁹ values.

I. AgH

There have been several studies on the $^1\Sigma^+$ ground state of AgH. Lee and McLean¹ carried out the first all-electron Dirac-Haree-Fock (DHF) calculation for AgH. They estimated that relativistic effects shrink the r_e by ~ 0.07 Å and enhanced the binding energy by 0.08 eV. Martin² has studied the ground state of AgH using the Breit-Pauli Hamiltonian. The effect of mass-velocity and Darwin terms were added using first-order perturbation. Hay and Martin⁴ also used their ECPs to calculate the ground state properties of AgH. The bond lengths obtained using all these procedures are somewhat longer than experimental values. Langhoff *et al.*⁹ made both all electron SCF/SDCI/CPF and the Hay-Wadt RECP MCPF calculations. The bond length obtained using a MCPF method in conjunction with the Hay-Wadt RECPs was found to be 0.04 Å longer than the experimental value. Similarly ω_e was found to be roughly 60 cm⁻¹ smaller than the experimental value. Langhoff *et al.*⁹ obtain r_e within 0.01 Å of the experimental value using a 20e correlated CPF + rel big basis approach.

As seen from Table IX, the CASSCF/SOCI-D method which correlated all 12 outer electrons yielded an r_e of 1.632 Å. This value is much improved compared to an $r_e = 1.656$ Å obtained by RECP SCF/MCPF⁹ method which correlated 12 electrons. The 20e CPF + rel big basis,⁹ however, yielded an r_e of 1.625 Å. This implies that the difference of 0.01 Å between our Davidson-corrected r_e of 1.632 Å and an experimental value of 1.62 Å is primarily due to the $(4s^2 4p^6)$ core-valence electron correlation effects. If we corrected our r_e by the $(4s^2 4p^6)$ core-valence correlation correction obtained by Langhoff *et al.* (-0.01 Å), we get an $r_e = 1.622$ Å in exact agreement with the experiment. The CASSCF/SOCI method yields a ω_e of 1761 cm⁻¹ in almost exact agreement with an experimental value of 1760 cm⁻¹. But the Davidson correction overshoots the ω_e . Our CAS/SOCI di-

TABLE IX. Spectroscopic constants of AgH.

State	R_e (Å)			ω_e (cm ⁻¹)			μ_e (D)		D_e (eV)		
	SOCI (SOCI-D)	MCPF (20e CPF)	Expt.	SOCI (SOCI-D)	MCPF (20e CPF)	Expt.	SOCI	MCPF	SOCI (SOCI-D)	MCPF	Expt. ^a
$^1\Sigma^+$	1.636 (1.625)	1.656 (1.628)	1.62	1745 (1770)	1703 (1731)	1759.9	3.06	2.95	2.20 (2.26)	2.22	2.39

^a The experimental D_0^0 (AgH) = 2.28 eV from Ref. 24 was corrected for zero-point correction to obtain D_e . The MCPF values from Ref. 9.

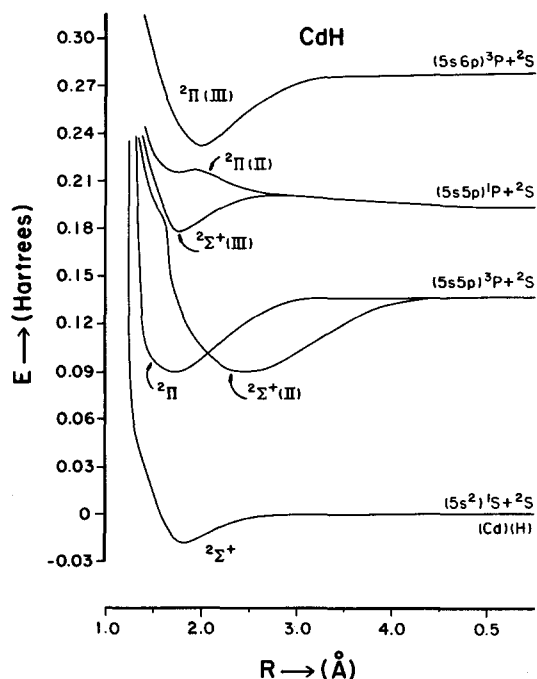


FIG. 1. Potential energy curves of electronic states of CdH.

pole moment of 3.1 D is slightly larger than the SCF/MCPF value of 2.95 D.

The present CASSCF/SOCI-D D_e of AgH is 2.20 eV compared to 2.22 eV obtained using the MCPF method.⁹ The CPF 20e + rel big basis yielded a higher D_e of 2.37 eV. Hence we conclude that a CASSCF/SOCI method together with RECPs yields results in excellent agreement with the most accurate calculations to date on AgH (Ref. 9) and in good agreement with the experiment.

J. CdH

The diatomic CdH has not been studied theoretically up to now. For this reason, we decided to carry out more extensive calculations on CdH. Figure 1 shows the potential energy curves of the $X^2\Sigma^+$ ground state, $B^2\Sigma^+(II)$, $C^2\Sigma^+(III)$, $A^2\Pi$, $2\Pi(II)$, and $2\Pi(III)$ excited states. Since Cd represents the transition point of transition metal to main group p block character, it is quite interesting to study the relative importance of $5s$ – $5p$ and $4d$ – $5s$ excitations.

We used two different sets of approaches to study the electronic states of CdH as mentioned in Sec. II. The first approach retained all 13 electrons keeping the $4d$, $5s$ orbitals

of Cd and the $1s$ orbital of hydrogen as active orbitals. Then SOCI calculations correlated these 13 outer electrons. This was very satisfactory for the $X^2\Sigma^+$ ground state as evidenced from the 13e-correlated spectroscopic constants of the $X^2\Sigma^+$ ground state in Table X.

Table X shows the spectroscopic constants of the ground state of CdH. The $X^2\Sigma^+$ ground state included correlation effects of 13 electrons using the SOCI method. As seen from Table X, the r_e of the $X^2\Sigma^+$ state is 1.75 Å, considerably longer than all TMHs in the second row. This is expected since bonding can be achieved only through $5s$ – $5p$ and core–valence excitations. The Davidson correction was found to increase the r_e and decrease the ω_e . As seen from Table X, the Davidson-corrected r_e of CdH is only 0.02 Å shorter than the experiment. It is interesting to note that higher-order quadruple excitations increase the bond length. The Davidson-corrected ω_e is a bit larger than the experimental value of 1337 cm^{−1}. The dipole moment of CdH is calculated as 0.5 D with Cd⁺H[−] polarity.

The D_e (CdH) is 0.59 eV at the 13e correlated SOCI method. The Davidson correction improves the D_e at most 0.01 eV. The experimental value of 0.68 eV is (~0.08 eV) larger than our SOCI-D value. This suggests significant weakening of this bond in moving from Ag to Cd mainly due to the closed shell $4d^{10}5s^2$ ground state of the Cd atom. The weakening of the bond also suggests some inert-pair ($5s^2$) effect arising from partial relativistic stabilization of the $5s^2$ shell. Note that ZnH has a D_0^0 value of 0.88 eV²⁴ and is thus more bound compared to CdH. We expect the relativistic inert-pair effect of the $6s^2$ shell to be significantly larger for HgH and hence the bonding would be considerably weaker for HgH [D_0^0 (HgH) = 0.37 eV²⁴].

Table XI shows the asymptotic energy separations of molecular states of CdH, their theoretical and experimental energies at the dissociation limit. As seen from Table XI, the 2Π , $2\Pi(II)$ and other excited states arise from the $5s$ – $5p$ excitation. Hence for these states it would be necessary to keep the $5p$ orbitals of Cd in the active space. Thus another set of CASSCF calculations which included $5s$, $5p$ orbitals of Cd and the $1s$ orbital of H in the active space were made. Excitations from the $4d$ were not allowed at the CAS-MCSCF stage but the $4d$ orbitals were allowed to relax. Then a FOCI approach which not only correlated the three valence electrons but also included an excitation of a single $4d$ electron in all possible ways into the external space was used to generate the potential energy curves in Fig. 1. This method includes both valence correlation effects and d correlation effects.

As seen from Table XI, the agreement of theoretical

TABLE X. Spectroscopic constants of the ground state of CdH.

State	R_e (Å)		ω_e (cm ^{−1})		T_e (cm ^{−1})	μ_e (D)	D_e (eV)	
	SOCI	Expt.	SOCI	Expt.	SOCI	SOCI	SOCI	Expt. ^a
$2\Sigma^+$	1.749 (1.761)	1.781	1604 (1524)	1337	0	0.5	0.59 (0.60)	0.68

^a From Ref. 24.

TABLE XI. Molecular states of CdH and theoretical and experimental energy separations at the dissociation limit.

		Theory	Expt. ^a
$^2\Sigma^+$	$(5s^2) ^1S_g + ^2S_g$	0.0	0.0
$^4\Pi, ^2\Pi, ^4\Sigma^+, ^2\Sigma^+$	$(5s5p) ^3P_u + ^2S_g$	29 745	31 200
$^2\Pi, ^2\Sigma^+$	$(5s5p) ^1P + ^2S$	42 579	43 692
$^4\Sigma^+, ^2\Sigma^+$	$(5s6s) ^3S + ^2S$...	51 484
$^4\Pi, ^2\Pi, ^4\Sigma^+, ^2\Sigma^+$	$(5s6p) ^3P + ^2S$	61 100	57 683

^a From Ref. 36.

asymptotic energy separations with the corresponding experimental values from Moore's table³⁶ is excellent considering that the high-lying states arise from Rydberg configurations of the Cd atom. This suggests that our basis sets and level of electron correlations are quite satisfactory for not only the $X^2\Sigma^+$ ground state but also several excited electronic states of CdH.

The potential energy curves of CdH in Fig. 1 show interesting trends. The $X^2\Sigma^+$ ground state is relatively less bound compared to some of the excited states. The crossing of the $^2\Sigma^+$ (II) state with the $^2\Pi$ state is very interesting. This would actually lead to an avoided crossing of the corresponding $\Omega = 1/2$ components in the presence of spin-orbit coupling. The RCI calculations made using the ground state orbitals of CdH yielded this behavior. However, the RCI calculations using the $^3\Sigma^-$ orbitals of CdH⁻ underestimated this mixing and hence the constants in Table XII are similar for the two spin-orbit states.

The spectroscopic constants of both the excited and $X^2\Sigma^+$ ground states obtained using the d -FOCI method are shown in Table XII. Since the $5p$ orbital of Cd was included in the active space of d -FOCI, the excited states are adequately represented in the d -FOCI procedure. However, the $X^2\Sigma^+$ ground state is not as well described as the full SOCI method which correlated both the $4d^{10}$ and $5s^2$ shells of Cd. Consequently, we conclude that d correlation effects are more significant for the $X^2\Sigma^+$ ground state of CdH, while $5s-5p$, $5s-6s$, $5s-6p$ excitations are more significant for the excited electronic states of CdH.

There are a few spectroscopic studies on CdH as summarized in Ref. 24, especially the one by Breckenridge and Callear²³ is worth mentioning. These studies have led to the characterization of A-X, B-X, and C-X systems. An emis-

sion system denoted as D→X has also been observed with $\nu_{0,0} = 44\,136\text{ cm}^{-1}$ by Breckenridge and Callear,²³ but the constants of the D state are not known. Based on Table XI, we suggest that a probable candidate for the D state is the $^2\Sigma^+$ (IV) state arising from $(5s6s) ^3S$ Rydberg state of Cd.

As seen from Table XII, the agreement of our theoretical constants with the known experimental values up to now is excellent. We note that for the ground state the D_e in Table X is superior since this value includes extensive d correlation effects while the constants in Table XII include d correlation effects to only first order.

The theoretical T_e 's for the excited states are especially in remarkable agreement with the experimental constants considering, for example, the $C^2\Sigma^+$ state arises from the $(5s6s) ^3S$ state of the Rydberg atom. But we are not surprised by this agreement since the basis set employed $(6s6p5d\,1f)$ is sufficiently flexible to represent the Rydberg states of the Cd atom arising from the $6s$ and $6p$ orbitals of Cd.

As seen from Table XII, our theoretical calculations fully support the earlier assignment of A-X, B-X, C-X systems to $A^2\Pi-X^2\Sigma^+$, $B^2\Sigma^+-X^2\Sigma^+$, and $C^2\Sigma^+-X^2\Sigma^+$ systems. It is noteworthy that the $B^2\Sigma^+$ has a long r_e as predicted by theory and also deduced from the B-X spectra. The $C^2\Sigma^+$ state is actually a Rydberg state.

The dipole moments of the electronic states of CdH are unknown up to now. Our theoretical calculations predict the $X^2\Sigma^+ \mu_e = 0.51\text{ D}$ with Cd⁺H⁻ polarity while the $A^2\Pi$ state has a significantly larger $\mu_e = 1.83\text{ D}$. It is interesting to note the dipole moment of the $B^2\Sigma^+$ state 1.1 D with Cd⁻H⁺ polarity. Consequently the B-X system involves considerable charge transfer from metallic to nonmetallic character. This is not surprising since the $B^2\Sigma^+$ state arises

TABLE XII. Spectroscopic constants of the ground and excited states of CdH.^a

State	r_e (Å)		ω_e (cm ⁻¹)		T_e (cm ⁻¹)		μ_e (D)	D_e (eV)	
	d-FOCI	Expt.	d-FOCI	Expt.	d-FOCI	Expt.	d-FOCI	d-FOCI	Expt.
$X^2\Sigma^+$	1.794	1.781	1298	1337	0	0	0.51	0.48	0.68
$A^2\Pi_{1/2}$	1.72	[1.669]	1592	1677	23 027	22 117	1.83		
$A^2\Pi_{3/2}$	1.722	[1.657]	1590	1758	23 919	23 116			
$B^2\Sigma^+$	2.433	2.39	967	[1000]	24 494	24 961			
$C^2\Sigma^+$	1.734	1.68	...	1567	42 794	[40 202]	- 1.1		
$^2\Pi$ (II)	1.75	...	1377	...	51 054	...			
$^2\Pi$ (III)	1.97	...	1796	...	54 810				

^a All experimental constants from Ref. 24. Numbers in square brackets are uncertain.

from the $(5s5p)^3P$ configuration of the Cd atom.

The ground state parameters of CdH have also been deduced through ESR spectra of CdH in Ar matrix at 4 K by Knight and Weltner.²² The A state of CdH was found to exhibit Λ -type doubling. We expect the $A^2\Pi_{1/2}$ component to exhibit Λ doubling through interaction of the $B^2\Sigma^+$ state. Note that $B^2\Sigma^+_{1/2}$ component is only 1847 cm^{-1} above the $A^2\Pi_{1/2}$ state and hence is the most probable candidate for the observed Λ doubling.

The $X^2\Sigma^+$ ground state of CdH arises predominantly from the $1\sigma^2 2\sigma^2 3\sigma\delta^4\pi^4$ configuration. The $B^2\Sigma^+$ state was found to be a Rydberg state at short internuclear distances. For $1.8 < r < 2.0\text{ \AA}$, the $B^2\Sigma^+$ state was found to be predominantly $1\sigma^2 2\sigma 3\sigma^2\delta^4\pi^4$ in character. At 2.5 \AA , it undergoes strong avoided crossing of $1\sigma^2 2\sigma 3\sigma^2\delta^4\pi^4$ (43%) with the $1\sigma^2 2\sigma 3\sigma 4\sigma\delta^4\pi^4$ (44%). Therefore, the long r_e in the $B^2\Sigma^+$ state arises from an avoided crossing of the $1\sigma^2 2\sigma 3\sigma^2\delta^4\pi^4$ configuration with the $1\sigma^2 2\sigma 3\sigma 4\sigma\delta^4\pi^4$ configuration. At very long distances, it is predominantly $1\sigma^2 2\sigma 3\sigma 4\sigma\delta^4\pi^4$ configuration so that it would dissociate into $(5s5p)^3P(\text{Cd}) + ^2S(\text{H})$. Consequently, the long-range minimum in the $B^2\Sigma^+$ state of CdH is attributed to this avoided crossing. The short-range shoulder in the $^2\Pi$ (Π) state also arises from an avoided crossing.

IV. RELATIVE TRENDS

Figure 2 shows the relative variation of the dipole moments of YH–CdH as one moves across the periodic table. As seen from Fig. 2, the dipole moments of Y and Zr are almost the same. The electronegativity of Zr is slightly larger than Y. This means that if the bond lengths of YH and ZrH are the same then the dipole moment of ZrH should be smaller than YH. But YH has considerably longer bond length (0.14 \AA) than ZrH. The bond elongation in YH should then compensate for the electronegativity difference between Y and Zr. The two effects cancel out and thus YH should have comparable dipole moment to ZrH. Hence the Langhoff *et al.*⁹, MCPF $\mu_e = 1.54\text{ D}$ for YH is too large and is inconsistent with both the YH–ZrH trend we obtain, and an experimental value of 1.8 D for YF.²⁶ In general the SCF/MCPF method tends to predict too ionic bonds.

The dipole moment of NbH and MoH are found to be significantly higher than ZrH. The r_e 's of NbH (1.787 \AA) and MoH (1.747 \AA) are comparable to the r_e of ZrH (1.811 \AA). This means that the ionic characters of NbH and MoH

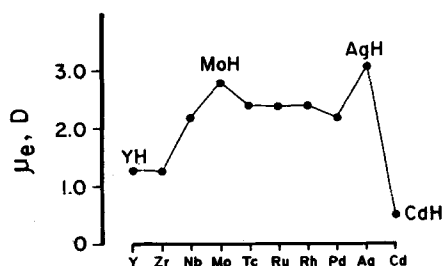


FIG. 2. Relative trend of the dipole moment (μ_e) of the second-row TMHs.

are larger than ZrH. The dipole moment of (TcH, RuH, RhH) trio form a collinear curve. There is a small drop in the dipole moment as one moves from Rh to Pd but this trend noticeably changes for AgH consistent with longer bond length of AgH compared to PdH and greater metallic character of Ag compared to Pd. The sharp drop in the μ_e of CdH compared to AgH is consistent with significant increase in the electronegativity of Cd compared to Ag.

The relative trend of our SOCI D_e 's together with available experimental data for MoH, RuH, RhH, PdH, AgH, and CdH are shown in Fig. 3. As seen from Fig. 3, our theoretical values mimic the experimental trend and are uniformly $0.1\text{--}0.2\text{ eV}$ below the experimental values with the exception of RhH as expected. But the experimental dissociation energies have an uncertainty of $\pm 0.2\text{ eV}$ for all hydrides except PdH for which a larger uncertainty of 0.26 eV exists. Among the second row TMHs, YH has the largest D_e while CdH has the smallest D_e .

A critical comparison of the D_e 's obtained using the CAS/SOCI method and SCF/MCPF procedure indicates that the agreement of the two procedures is very good for YH, ZrH, and NbH. However, our Davidson-corrected D_e (MoH) is 0.11 eV larger than the SCF/MCPF method but agrees with the experiment. Similar discrepancy of 0.22 and 0.16 eV are noted for TcH and RhH, respectively. We are not surprised by the significantly smaller D_e predicted by the SCF/MCPF method since electron correlation effects tend to be very significant for the molecular well of the $^5\Sigma^+$ state of TcH while at the dissociation limit [$\text{Tc}(^7S) + \text{H}(^2S)$], correction effects tend to be smaller. This means that our D_e for $^7\Sigma^+$ state should agree with the SCF/MCPF method but should be larger for the $^5\Sigma^+$ state. This is in fact what we find as seen in Table V.

The D_e 's of RuH obtained using the SCF/MCPF method also differ from our CAS/SOCI values. As noted before for RuH, we believe that this is mainly a consequence of a different ground state obtained using the SCF/MCPF method. The agreement in the D_e (AgH) between the SOCI and MCPF methods is, however, very good.

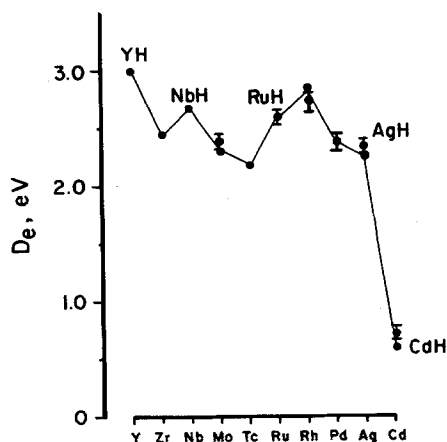


FIG. 3. Relative trend of the D_e 's of the second-row TMHs. (Experimental values with error bars from Ref. 27 corrected for zero-point energy are included for comparison. The experimental points are not joined since at present bond energies of only CdH, AgH, PdH, RhH, RuH, and MoH exist.)

V. CONCLUSION

In this investigation, we studied low-lying electronic states of YH–AgH and six electronic states of CdH. The potential energy curves and spectroscopic constants of CdH were also obtained. We conclude that $(4s^2 4p^6 4d^9 5s^2)$ RECPs of La John *et al.*³⁰ give r_e , ω_e , and D_e values in very good agreement with experimental constants when available. A particular superior feature of the La John *et al.* RECPs is that they include spin–orbit effects. The accurate CASSCF/SOCI study in conjunction with large $(6s6p5d\ 1f)$ basis sets yielded μ_e 's approximately 0.2–0.3 D smaller than the previous SCF/MCPF calculation.⁹ Our μ_e of YH is supported by a recent experimental measurement of YF.²⁶ Our ω_e 's of the $^2\Delta$ state of ZrH and $^5\Delta$ state of NbH differed significantly from the previous SCF/MCPF study.⁹ The present D_e 's are much improved and in closer agreement with the experiment. Our descriptions of NbH and RuH differ significantly from the previous SCF/MCPF study⁹ because (i) previous study did not consider the $^5\Pi$ and $^4\Sigma$ states of NbH and RuH, respectively, and (ii) previous study neglected spin–orbit effects. Nearly degenerate electronic states were obtained as candidates for the ground states of NbH, TcH, and RuH. The $^5\Pi_3$ and $^5\Delta_3$ states of NbH were found to undergo an avoided crossing. The relative trend of our D_e 's mimic the experimental trend for the dissociation energies of MoH, RuH, RhH, PdH, AgH, and CdH. Our calculations confirm the previous assignment of the observed spectra of CdH and explain the origin of the long-range minimum in the $B\ ^2\Sigma^+$ state of CdH. Our theoretical spectroscopic constants of X , A , B and C states of CdH were found to be in excellent agreement with experimental constants.

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