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Electronic states and potential energy surfaces of RhH

K. Balasubramanian[a] and Dai-Wei Liao

Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604

Complete active space MCSCF (CASSCF) followed by first-order configuration interaction (FOCI) calculations are carried out on nine λ–s states of RhH. In addition, relativistic configuration interaction (RCI) calculations which include spin–orbit interaction are carried out on 19 ω–ω states of RhH. The potential energy surfaces and spectroscopic properties $(R_e, T_e, \omega_e, D_e, \mu)$ are computed for the electronic states of RhH. The calculated CASSCF/FOCI dipole moments of both the ground and excited states reveal considerable ionic character (Rh^+H^-) with the exception of the $^1\Delta$ state which is somewhat less ionic. The spin–orbit effects are found to be quite significant for the electronic states of RhH. The spin–orbit contaminations of the low-Ω states $[1,1(II),1(III),1(IV),0^+]$ are found to be appreciable. The spin–orbit splittings of low-lying electronic states were found to be 1200–3200 cm^{-1}.

I. INTRODUCTION

The investigation of transition metal hydrides is of considerable importance from both theoretical and experimental standpoints. Theoretically, one could gain considerable insight into the nature of the metal–hydrogen bond, the participation of the d orbitals in bonding, and the spectroscopic properties of low-lying electronic states.

Relativistic effects are especially significant for molecules containing heavy atoms.[1-5] The importance of relativistic configuration interaction calculations (RCI) which take into account both the effects of correlation and spin–orbit interaction simultaneously for molecules containing very heavy atoms has been demonstrated in recent years.[6-14] The effect of spin–orbit interaction on second row transition metal hydrides has not been investigated to date with the exception of PdH[14] for which it was shown that these effects are quite significant.

The only theoretical investigation on RhH to date is that of Langhoff *et al.*[15] who have studied three electronic states of RhH using SCF/SDCI, MCPF, and CPF schemes. While these authors[15] have incorporated Darwin and mass-velocity corrections for these states using the relativistic effective core potentials of Hay and Wadt, they ignore the spin–orbit interaction. The present investigation on RhH is aimed at studying many electronic states (9 λ–s states, 19 ω–ω states) including spin–orbit effects. We carry out complete active space MCSCF (CASSCF) followed by first-order configuration interaction (FOCI) calculations. The spin–orbit effects are introduced through a variational relativistic CI scheme. Thus both correlation and relativistic effects including spin–orbit interaction are introduced to a very high order.

The bond energies of RhH have been experimentally measured by a few authors.[16-18] The RhH molecule is one of the many species found in the weighted column densities of many molecules in an oxygen-rich star[19] for which the laboratory spectrum is not known to date. Thus the present theoretical calculations would be of use in the spectroscopic investigation of this system.

The spectroscopic properties calculated in this investigation include R_e, T_e, ω_e, D_e, and dipole moments. The Mulliken population analysis of the FOCI natural orbitals are also reported. The potential energy surfaces of nine low-lying electronic states are calculated. Section II describes our method of investigation while Sec. III contains results and discussions.

II. METHOD OF CALCULATIONS

The ground state of the Rhodium atom is the $^4F_{9/2}$ state arising from the outer $4d^8 5s^1$ electronic configuration.[20] The spin–orbit splitting of the ground state $(^4F_{9/2} - 4F_{3/2})$ is about 3473 cm^{-1}. There are 10 j–j states with j values ranging from 9/2–3/2 below 10 000 cm^{-1} for the Rh atom. This in itself reveals the complexity of the problem since many low-lying electronic states are possible for RhH.

Table I shows a few low-lying electronic configurations

TABLE I. λ–s and ω–ω arising from a few low-lying MO configurations of RhH.

Configuration	λ–s state	ω–ω state
$1\sigma^2 2\sigma\delta^3\pi^4$	$^3\Delta$	3,2,1
	$^1\Delta$	2
$1\sigma^2 2\sigma\delta^4\pi^3$	$^3\Pi$	2,1,0$^+$,0$^-$
	$^1\Pi$	1
$1\sigma^2 2\sigma^2\delta^3\pi^3$	$^3\Phi$	4,3,2
	$^1\Phi$	3
	$^3\Pi$	2,1,0$^+$,0$^-$
	$^1\Pi$	1
$1\sigma^2\delta^4\pi^4$	$^1\Sigma^+$	0$^+$
$1\sigma^2 2\sigma^2\delta^2\pi^4$	$^3\Sigma^-$	0$^+$,1
	$^1\Gamma$	4
	$^1\Sigma^+$	0$^+$
$1\sigma^2 2\sigma^2\delta^4\pi^2$	$^3\Sigma^-$	1,0$^+$
	$^1\Delta$	2
	$^1\Sigma^+$	0$^+$

[a] Alfred P. Sloan Fellow; Camille and Henry Dreyfus Teacher–Scholar.

TABLE II. Basis sets employed for the Rh atom.[a]

	Rh	
	STO	GTO
s	2.1025(5)	0.429 1
	1.1889(5)	0.157 1
		0.045 89
p	0.9000(5)	0.10
		0.05
d	3.8666(4)	2.900 0
	1.9070(4)	(0.089 584)
		1.435 0
		(0.393 999)
		0.534 0
		0.163 8

[a] The numbers in the parentheses for the STO exponents are the principal quantum number, but the one under the GTO exponents are contraction coefficients.

of RhH, the λ–s and ω–ω states arising from them. In that table the δ and π orbitals are nonbonding Rh d orbitals. The exact nature of the 1σ and 2σ orbitals can be determined through calculations, although qualitatively, they are likely to be a mixture of Rh $d\sigma$, Rh s, and H s orbitals. The spin–orbit splitting and contamination are certainly nonnegligible for RhH and thus both λ–s and ω–ω states need to be calculated.

We employ relativistic effective core potentials (RECP) reported by LaJohn et al.[21] for the rhodium atom. The $4d^8 5s^1$ outer shell was explicitly retained in the calculations. These authors have also optimized a valence Gaussian basis set for the rhodium atom. The $(3s4d)$ primitive basis was contracted to a $(3s3d)$ basis set shown in Table II. In addition, two sets of p-type functions were added with the exponents of 0.10 and 0.05. The resulting basis can be described as a $(3s3d\,2p)$ basis set. For the hydrogen atom, we employ the van Duijneveldt's[22] $(5s/3s)$ basis set augmented by a set of p-type polarization functions with the exponent of 0.9. A double-zeta Slater-type basis (STO) was also optimized for relativistic configuration interaction codes to calculate the effect of spin–orbit interaction. The double-zeta STO basis set is also shown in Table II. For the hydrogen atom, the STO basis set employed earlier in PdH[14] calculations was used here.

The orbitals for CI calculations were generated using a complete active space MCSCF (CASSCF) scheme. In this method, the nine outer electrons of Rh (d^8s^1) and the single electron of hydrogen atom are distributed in all possible ways among the primary space of active orbitals referred to as the internal space. The molecule was oriented along the z axis. The calculations were carried out in the C_s point group mainly for computational convenience since excited states are higher roots of two spatial symmetries in the C_s group. The internal space in CASSCF included the strongest occupied orbitals of the atoms at infinite separation, namely the $4d$ and $5s$ orbitals of Rh and the $1s$ orbital of H. In the C_s group, these orbitals span $5a'$ and $2a''$ representations. The

ten outer electrons were distributed among the active orbitals in all possible ways. The CASSCF calculations included about 90–110 CSFs.

The configuration interaction calculations carried out were first-order CI (FOCI) calculations. The FOCI calculation included all configurations in the CASSCF plus the configurations generated by distributing nine electrons in the internal space of orbitals and one electron in the orthogonal external space in all possible ways. The FOCI calculations included 6500 and 9500 CSFs in the C_s group for the singlet and triplet states, respectively.

The spin–orbit effects are introduced through a relativistic configuration interaction scheme (RCI). This is a multireference singles and doubles scheme in which both spin–orbit and correlation effects are introduced simultaneously. In general, in RCI calculations, all λ–s states which have the same ω–ω symmetry are mixed in a variational scheme. For RhH all low-lying λ–s states which give rise to a ω–ω state of a given symmetry are included as reference configurations depending on the Ω value of the state. The RCI calculations included about 2–16 reference configurations. The RCI calculations were carried out after a SCF calculation using the double-zeta STO basis in Table II. Two sets of CI calculations were carried out one with and the other without spin–orbit interaction. The difference in the spectroscopic properties and energies obtained with and without spin-orbit corrections measure the effect of this term and are thus introduced as corrections to the CASSCF/FOCI properties obtained without the spin–orbit term. This procedure ensures that both spin–orbit and correlation effects are taken into account accurately. The CASSCF/FOCI calculations were carried out using one of the present authors (K. B.) modified version of ALCHEMY II codes[23] to include relativistic effective core potentials as described in Ref. 24. The RCI calculations were carried out using the K. B.'s enhanced version of the code developed earlier based on the method in Ref. 13.

III. RESULTS AND DISCUSSIONS

Table III shows the spectroscopic properties $(R_e, T_e, \omega_e, D_e)$ and the dipole moments (μ) of nine λ–s states calculated using the CASSCF/FOCI scheme. As one can see from Table III, the calculated ground state of RhH in the absence of spin–orbit interaction is the $^3\Delta$ state arising

TABLE III. Spectrostopic properties of RhH in the absence of spin–orbit interaction.

State	R_e(Å)	T_e(cm^{-1})	ω_e(cm^{-1})	D_e(eV)	μ (D)[a]
$^3\Delta$	1.54	0	2027	2.83	2.541
$^1\Sigma^+$	1.56	3 372	2052	2.91	2.644
$^3\Phi$	1.61	4 159	1822	2.31	3.387
$^3\Pi$	1.62	4 639	1779	2.25	3.345
$^3\Sigma^-$	1.61	4 659	2132	2.25	3.222
$^1\Pi$	1.58	7 698	1915	2.38	2.797
$^3\Pi$(II)	1.60	11 229	1754	1.86	2.998
$^1\Delta$	1.50	14 547	2172	1.56	1.735
$^1\Gamma$	1.58	16 918	1892	1.47	3.198

[a] Polarity is M$^+$H$^-$.

FIG. 1. Potential energy curves of nine low-lying λ–s states of RhH in the absence of spin–orbit interaction.

TABLE IV. Spectroscopic properties of low-lying states of RhH including spin–orbit effects.

State	R_e (Å)	T_e (cm^{-1})	ω_e (cm^{-1})	D_e (eV)
$^3\Delta_3$	1.54	0	2028	2.87
$^3\Delta_2$	1.56	527	1939	2.81
$^3\Delta_1$	1.59	1 377	1755	2.70
$^3\Phi_4$	1.61	3 613	1822	2.42
$^1\Sigma_0^+$	1.56	4 155	2044	2.35
$^3\Pi_1$	1.63	4 667	1761	2.29
$^3\Pi_2$	1.62	5 157	1779	$\cdots$
$^3\Phi_3$	1.61	5 201	1822	$\cdots$
$^3\Sigma_0^-$	1.61	5 843	2139	$\cdots$
$^3\Pi_0^-$	1.62	6 227	1778	$\cdots$
$^3\Pi_0^+$	1.62	6 228	1778	$\cdots$
$^3\Sigma_1^-$	1.60	6 447	2146	$\cdots$
$^3\Phi_2$	1.61	6 826	1822	$\cdots$
$^1\Pi_1$	1.58	8 817	1926	$\cdots$
$^3\Pi_2$ (II)	1.60	11 736	1752	$\cdots$
$^3\Pi_0^+$ (II)	1.60	12 810	1753	$\cdots$
$^3\Pi_0^-$ (II)	1.60	12 830	2189	$\cdots$
$^1\Delta_2$	1.50	15 697	2183	$\cdots$
$^1\Gamma_4$	1.58	17 990	1892	$\cdots$

from the $1\sigma^2 2\sigma\delta^3\pi^4$ electronic configuration. The calculated r_e, ω_e, and μ values in Table III for the $^3\Delta$, $^3\Pi$, and $^3\Phi$ states are between the SCF/SDCI and MCPF results reported by Langhoff et al.[15] recently for these states. The T_e values are, however, more sensitive to correlation as seen from Table III. The SCF/CI calculations of Langhoff et al.[15] predict nearly degenerate $^3\Pi$ and $^3\Phi$ excited states with a T_e value of ~ 6500 cm^{-1}. Note that $^3\Pi$ and $^3\Sigma^-$ states as seen from both Table III and Fig. 1 are almost degenerate. Figure 1 shows the calculated potential energy surfaces for nine low-lying λ–s states considered here. Among these, four electronic states dissociate to the $^4F + {}^2S$ ground state atoms while the other five electronic state dissociate into the excited states of Rh atom.

Table IV shows the spectroscopic properties of RhH corrected for spin–orbit effects. In Table IV, we show the spectroscopic properties of 19 electronic states of RhH. The ground state including spin–orbit interaction is calculated to be $^3\Delta_3$. The spin-orbit splitting of the ground state ($^3\Delta_3 - {}^3\Delta_1$) is roughly 1400 cm^{-1}. Note that the $^3\Delta$ state is an inverted triplet since it arises from the $1\sigma^2 2\sigma 1\pi^4 1\delta^3$ configuration. As one can see from Table IV, the spin–orbit splittings of excited states are quite large in general. In fact, the spin-orbit interaction causes different ordering of excited electronic states. The largest spin–orbit splitting is found for the $^3\Phi$ state which is 3213 cm^{-1}. This splitting is comparable to the rhodium $^4F_{9/2} - {}^4F_{3/2}$ atomic splitting which is about 3473 cm^{-1}.[20] The $^3\Pi_1$ state comes out to be lower then $^3\Pi_2$ contrary to the usual inverted ordering primarily because of the off-diagonal spin–orbit contamination with $^3\Sigma_1^-$ which lowers the $^3\Pi_1$ state relative to $^3\Pi_2$.

The spin–orbit effects make somewhat smaller contributions to R_e. The shifts in r_e are less than 0.05 Å, in general.

However, the ω_e values are altered substantially especially for the states with low-Ω quantum numbers since these states are contaminated substantially with other λ–s states due to spin–orbit mixing. The dissociation energies are decreased for some electronic states ($^3\Delta_2$,$^3\Delta_1$,$^1\Sigma^+$) while they are increased slightly for the $^3\Delta_3$ and $^3\Pi_1$ states. The spin–orbit interaction could also change the dipole moments although we have not studied this aspect in this investigation.

There are no experimental electronic spectra reported yet on RhH. From the results in Tables III and IV, it seems that many dipole-allowed electronic transitions are possible below 17 000 cm^{-1}. As mentioned in the Introduction, there are experimental bond energies reported on RhH. The experimental D_0^0 for the Rh–H bond energy reported by Tolbert and Beauchamp[16] is about 50 ± 5 kcal/mol although these authors have assumed the ground state of RhH to be $^3\Phi$ which disagrees with our results in Tables III and IV. The experimental D_e of about 2.56 eV, however, is in very good agreement with our calculated results.

Next, we discuss the nature of low-lying electronic states of RhH and the nature of Rh-H bond in these states. Table V shows the important configurations contributing to the FOCI wave function of the electronic states of RhH in the absence of spin-orbit interaction. The $^3\Delta$, $^3\Phi$, and $^1\Gamma$ are the only states for which the leading configuration makes a contribution $\geqslant 90\%$. All other states are substantially mixed with two or more configurations indicating the importance of a MCSCF treatment for these states. The 1σ orbital of the $^3\Delta$ ground state is a mixture of Rh s, Rh $d_{x^2 + y^2 - 2z^2}$, and H s. The contribution of the H s is greater for the 1σ orbital than the 2σ orbital. The 2σ orbital is more of Rh s and $d_{x^2 + y^2 - 2z^2}$. The δ and π orbitals are nonbonding Rh d orbitals. As we discuss later the overall gross Rh d population of the σ orbitals of the ground state is about 1.10 while the Rh s population is about 0.76.

TABLE V. Contributions (percent) of various electronic configuration in the FOCI wave functions of the electronic states of RhH near R_e without spin–orbit interaction.

State	Distance (Å)	Electronic configurations (percent of contributions)
$^3\Delta$	1.55	$1\sigma^2 2\sigma\delta^3\pi^4(96\%)$
$^1\Sigma^+$	1.55	$1\sigma^2\delta^4\pi^4(64\%),1\sigma^2 2\sigma^2\delta^2\pi^4(30\%)$
$^3\Phi$	1.60	$1\sigma^2 2\sigma^2\delta^3\pi^3(94\%)$
$^3\Pi$	1.60	$1\sigma^2 2\sigma^2\delta^3\pi^3(52\%),1\sigma^2 2\sigma\delta^4\pi^3(41\%)$
$^3\Sigma^-$	1.60	$1\sigma^2 2\sigma^2\delta^2\pi^4(69\%),1\sigma^2 2\sigma^2\delta^4\pi^2(26\%)$
$^1\Pi$	1.60	$1\sigma^2 2\sigma\delta^4\pi^3(54\%),1\sigma^2 2\sigma^2\delta^3\pi^3(37\%)$
$^3\Pi$ (II)	1.60	$1\sigma^2 2\sigma\delta^4\pi^3(49\%),1\sigma^2 2\sigma^2\delta^3\pi^3(40\%)$
$^1\Delta$	1.50	$1\sigma^2 2\sigma\delta^3\pi^4(86\%),1\sigma^2 2\sigma^2\delta^4\pi^2(5\%)$
$^1\Gamma$	1.60	$1\sigma^2 2\sigma^2\delta^2\pi^4(90\%)$

Table VI shows the percentage contributions of various λ–s states in the ω–ω states of RhH as obtained from relativistic CI wave functions. Table VI indicates the extent of spin–orbit contaminations (mixings of λ–s states of different symmetry). The general trend is that the high Ω states such as $^3\Delta_3$, $^3\Phi_4$, $^3\Phi_3$, and $^1\Gamma_4$ are pure states. The low-Ω states such as $^3\Delta_2$, $^3\Delta_1$, $^3\Pi_1$, $^3\Sigma_1^-$, etc., are substantially contaminated by spin–orbit interaction. Note that the $^3\Delta_1$–$^3\Pi_1$–$^3\Sigma_1^-$–$^1\Pi_1$ mixings are significant for the 1 states. Thus the properties of 1 and 2 states cannot be calculated neglecting the spin–orbit term. The $^1\Phi$–$^3\Phi$ mixing in the $^3\Phi_3$ state was found to be negligible. As one can see from both Table V and VI the $^3\Pi$ state is heavily mixed with $\sigma\pi^3$ and $\delta^3\pi^3$ configurations. The triplet–singlet mixing was found to be small in the Π and Δ states (i.e., $^3\Pi_1,^1\Pi_1,{}^3\Delta_2,^1\Delta_2$). The substantial changes in the ω_e values in Table IV for some of

the ω–ω states due to spin–orbit coupling can be correlated with the spin–orbit contaminations seen in Table VI. It must also be emphasized that the electronic dipole and transition moments of contaminated states would be substantially different from the FOCI values obtained without spin–orbit interaction. Thus the dipole moments of the states reported in Table III contaminated heavily by spin–orbit term are somewhat less accurate.

The Mulliken populations (gross, net, and overlap) obtained from the FOCI-natural orbitals of the electronic states of RhH are shown in Table VII. We subtracted the $x^2 + y^2 + z^2$ population from the d and added it to the s population in Table VII. The gross d populations of the $^3\Delta$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ states are between 8.0–9.0 indicating mixing of the two low-lying Rh $4d^8 5s^1$ and $4d^9$ atomic states. Note that this mixing is particularly large for the $^1\Sigma^+$ state for

TABLE VI. Contributions (percent) of various λ–s states to the ω–ω states of low-lying states of RhH.

ω–ω state	Distance (bohr)	λ–s states and their contributions
$^3\Delta_3$	3.12	$^3\Delta(94\%,\sigma\delta^3)$
$^3\Delta_2$	3.12	$^3\Delta(84\%,\sigma\delta^3),{}^3\Pi(4\%\ \sigma\pi^3,4\%\ \delta^3\pi^3),$ $^3\Phi(2\%,\delta^3\pi^3),{}^1\Delta(0.3\%,\sigma\delta^3)$
$^3\Delta_1$	3.12	$^3\Delta(72\%,\sigma\delta^3),{}^3\Pi(9\%\ \sigma\pi^3,8\%\ \delta^3\pi^3)$ $^3\Sigma^-(1.7\%\ \pi^2,0.9\%\ \delta^2),{}^1\Pi(1.5\%\ \sigma\pi^3,$ $0.6\%\ \delta^3\pi^3)$
$^3\Phi_4$	3.12	$^3\Phi(94\%,\delta^3\pi^3)$
$^1\Sigma_0^+$	3.12	$^1\Sigma^+(63\%\ \sigma^2,26\%\ \delta^2),{}^3\Sigma^-(5\%,\delta^2)$
$^3\Pi_1$	3.02	$^3\Pi(34\%\ \delta^3\pi^3,28\%\ \sigma\pi^3),$ $^3\Sigma^-(16\%\ \delta^2,15\%\ \pi^2)$ $^1\Pi(0.7\%\ \sigma\pi^3,0.003\%\ \delta^3\pi^3)$
$^3\Pi_2$	3.12	$^3\Pi(48\%\ \delta^3\pi^3,46\%\ \sigma\pi^3)$
$^3\Phi_3$	3.12	$^3\Phi(94\%,\delta^3\pi^3)$
$^3\Sigma_0^-$	3.12	$^3\Sigma^-(88\%,\delta^2),{}^1\Sigma^+(5\%,\delta^2)$
$^3\Pi_{0^-}$	3.12	$^3\Pi(48\%\ \delta^3\pi^3,46\%\ \sigma\pi^3)$
$^3\Pi_{0^+}$	3.12	$^3\Pi(48\%\ \delta^3\pi^3,46\%\ \sigma\pi^3)$
$^3\Sigma_1^-$	3.12	$^3\Sigma^-(29\%\ \pi^2,26\%\ \delta^2),$ $^3\Pi(20\%\ \delta^3\pi^3,18\%\ \sigma\pi^3)$
$^3\Phi_2$	3.12	$^3\Phi(94\%,\delta^3\pi^3)$
$^1\Pi_1$	3.12	$^1\Pi(83\%\ \sigma\pi^3,6\%\ \delta^3\pi^3)$
$^3\Pi_2$ (II)	3.21	$^3\Pi(49\%\ \sigma\pi^3,43\%\ \delta^3\pi^3)$
$^3\Pi_{0^+}$ (II)	3.59	$^3\Pi(48\%\ \sigma\pi^3,40\%\ \delta^3\pi^3)$
$^3\Pi_{0^-}$ (II)	3.59	$^3\Pi(48\%\ \sigma\pi^3,40\%\ \delta^3\pi^3)$
$^1\Delta_2$	3.02	$^1\Delta(88\%,\sigma\delta^3),{}^3\Delta(0.4\%,\sigma\delta^3)$
$^1\Gamma_4$	3.12	$^1\Gamma(95\%,\delta^2)$

TABLE VII. Mulliken population analysis of electronic states of RhH.

State	Net Population Total Rh	H	Rh(s)	Rh(p)	Rh(d)	Gross Population Total Rh	H	Rh(s)	Rh(p)	Rh(d)	Overlap population
$^3\Delta$	8.61	0.77	0.58	0.02	7.97	8.92	1.08	0.76	0.05	8.10	0.63
$^1\Sigma^+$	8.57	0.80	0.37	0.02	8.12	8.89	1.11	0.56	0.05	8.27	0.62
$^3\Phi$	8.53	0.77	0.88	0.02	7.61	8.88	1.12	1.14	0.06	7.68	0.70
$^3\Pi$	8.54	0.79	0.69	0.02	7.82	8.88	1.12	0.91	0.06	7.90	0.66
$^3\Sigma^-$	8.54	0.76	0.94	0.02	7.55	8.89	1.11	1.19	0.06	7.64	0.70
$^1\Pi$	8.58	0.78	0.65	0.02	7.86	8.90	1.10	0.87	0.05	7.99	0.64
$^3\Pi$ (II)	8.59	0.78	0.65	0.03	7.91	8.91	1.09	0.84	0.07	8.00	0.64
$^1\Delta$	8.73	0.73	0.71	0.02	8.04	9.00	1.00	0.79	0.05	8.16	0.54
$^1\Gamma$	8.53	0.77	0.91	0.02	7.50	8.88	1.12	1.19	0.07	7.62	0.70

which the gross d population is 8.27. For the $^3\Phi$ state, however, the d population is somewhat small (7.68) implying mixed d character ($4d^7 5s^2$ and $4d^8 5s^1$). The total gross Rh population for all the electronic states except $^1\Delta$ are lower than nine and the H population is higher than 1.0 indicating ionic character (Rh^+H^-). The calculated dipole moment trends are similar to the Mulliken population trends although, the dipole moment depends not only on the charges but their separations as well, and thus would depend on the bond lengths of the states also. The contribution of the p atomic orbitals of Rh is relatively small. The overlap between Rh and H is largest for the $^3\Phi$ and $^3\Sigma^-$ states and smallest for the excited $^1\Delta$ state. The contribution of the Rh(s) is between half and three-fourths of the atomic ground state occupancy ($4d^8 5s^1$) for most of the states except the $^3\Phi$, $^3\Sigma^-$, and $^1\Gamma$ states for which the s population is greater than unity.

IV. CONCLUSION

In this investigation, we studied 9 low-lying λ–s states and 19 ω–ω states of RhH. Both spectroscopic properties (R_e, ω_e, T_e, and D_e) and the dipole moments of some of the low-lying states were calculated. The potential energy surfaces of nine λ–s states are also reported. The spin–orbit effects and spin–orbit contaminations were found to be substantial for the low-lying states of RhH. The Mulliken population analysis of the low-lying states reveal substantial ionic character (Rh^+H^-). The population analysis of $^3\Delta$, $^1\Sigma^+$, $^1\Pi$, and $^1\Delta$ states reveal that both $4d^8 5s^2$ and $4d^9$ states of Rh atom contribute to these states while the $^3\Phi$ state had a different gross Mulliken population (7.68). The calculated dissociation energies are in good agreement with experimental results but there are no experimental electronic spectra for comparison of calculated spectroscopic properties.

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