Low-Lying Singlet and Triplet Electronic States of RhB

Antonio Carlos Borin* and João Paulo Gobbo

Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508−900, São Paulo, SP, Brazil

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The low-lying $X^1\Sigma^+$, $a^3\Delta$, $A^1\Delta$, $b^3\Sigma^+$, $B^1\Pi$, $c^3\Pi$, $C^1\Phi$, $D^1\Sigma^+$, $E^1\Pi$, $d^3\Phi$, and $e^3\Pi$ electronic states of RhB have been investigated at the ab initio level, using the multistate multiconfigurational second-order perturbation (MS-CASPT2) theory, with extended atomic basis sets and inclusion of scalar relativistic effects. Among the eleven electronic states included in this work, only three (the $X^1\Sigma^+$, $D^1\Sigma^+$, and $E^1\Pi$ states) have been investigated experimentally. Potential energy curves, spectroscopic constants, dipole moments, binding energies, and chemical bonding aspects are presented for all electronic states.

1. Introduction

RhB was observed for the first time by Chowdhury and Balfour,[1] using laser induced fluorescence in the range of 430−550 nm. From the analysis of the experimental results, the authors concluded that the ground electronic state possesses $^1\Sigma^+$ symmetry ($R_0 = 1.691$ Å, $\Delta G_{1/2} = 920$ cm^{-1}), characterized by the $10\sigma^2 11\sigma^2 5\pi^4 2\delta^4$ electronic configuration, with the Rh and B atoms bonded by a triple bond. In addition, an excited electronic state of $^1\Sigma^+$ symmetry (the so-called $[20.0]^1\Sigma^+$ state) was also proposed, located at about 20 000 cm^{-1} above the ground state, with $R_0 = 1.870$ Å and $\Delta G_{1/2} = 628$ cm^{-1}, for which the electronic nature could not be determined unequivocally from the experimental data. Besides that, very recently, Chowdhury and Balfour[2] reported a new band system with (0,0) at 20 110 cm^{-1}, which was attributed to a $^1\Pi - X^1\Sigma^+$ electronic transition. Again, the electronic nature of the $^1\Pi$ state, which was coined as the $[20.1]^1\Pi$ state, could not be determined from the analysis of the experimental data.

On the basis of results obtained by the CASSCF/MS-CASPT2 method[3−7], we[8] showed that the $[20.0]^1\Sigma^+$ state derives from the RhB ground state by a single electronic transition from the 11σ bonding valence molecular orbital (VMO) to the 12σ antibonding orbital ($11\sigma \rightarrow 12\sigma$). We also found a $^1\Delta$ excited state (the $[9.0]^1\Delta$ state) 9221 cm^{-1} above the $X^1\Sigma^+$ state, with $R_0 = 1.786$ Å, $\Delta G_{1/2} = 792$ cm^{-1}, and dominated by a single electronic configuration ($...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1$) obtained by a single excitation ($2\delta \rightarrow 12\sigma$) from the ground state wave function. Recently, Chowdhury and Balfour[2] employed our description of the $[9.0]^1\Delta$ state to analyze certain features of the experimental electronic spectrum of RhB.

Except for the above-mentioned studies,[1,2,8] no other experimental or theoretical investigations have been published. In order to gain further insight into the structural and spectroscopic properties of RhB, we have carried out a theoretical study focusing our attention on the first two atomic dissociation channels. The first corresponds to the adiabatic coupling of the two atoms in their atomic ground states (B ($^2P^\circ$ ($2s^2 2p$)) and Rh (^4F ($4d^8(^3F)5s$))),[9] and the second involves the boron atom in its ground state and the rhodium atom in the first excited state (Rh (^2D ($4d^9$))), located 0.34 eV (*J*-averaged value) above the ground level. Among all possible 42 molecular electronic states, 24 ($^{3,5}\{\Sigma^+, \Sigma^-(2), \Pi(3), \Delta(3), \Phi(2), \Gamma\}$) dissociate into the ground state atoms, while the others ($^{1,3}\{\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(2), \Phi\}$) correlate with the second atomic dissociation channel. After preliminary calculations, we have found that the singlet and triplet states are well-separated from the quintuplets. The main purpose of this work is to give a detailed account of the low-lying singlet and triplet electronic states of RhB (11 $\Lambda - S$ electronic states), by means of potential energy curves, spectroscopic constants, dipole moments, binding energies, and chemical bonding analysis.

2. Methodology

The CASSCF/MS-CASPT2 (multistate multiconfigurational second-order perturbation)[3−7] approach was employed to generate multiconfigurational wave functions. At the CASSCF (complete active space (CAS) SCF method) step, the active space comprises the Rh 4d, 5s and B 2s, 2p orbitals and electrons (12 electrons in 10 orbitals), keeping the Rh 4s and 4p electrons inactive. For the CASPT2 calculations, the zeroth-order Hamiltonian suggested by Ghigo et al.,[10] with a shift parameter of 0.25 Hartree, was employed and the Rh 4s and 4p electrons were included in the active space; that is, the Rh semi-core electrons were correlated at the CASPT2 level. The Rh and B core electrons were kept frozen. As we have shown before,[11] multireference configuration interaction calculations are not feasible with such active space.

Intruder state problems were treated using an imaginary shift[12] of 0.1 Hartree. The Douglas−Kroll−Hess (DKH) approximation[13,14] was employed to take into account scalar relativistic effects. Quadruple-ζ atomic ANO-RCC[15] basis sets were employed for describing the atomic species; namely, the Rh atom is described by the primitive 21s15p10d6f4g2h set contracted to 8s7p5d3f2g1h, and the boron atom is described with the primitive set of 14s9p4d3f functions contracted to 5s4p3d2f.[16]

All calculations were carried out with the software MOLCAS-6.4,[17] using the C_2 point group symmetry. The singlet states were described by including the first four low-lying states belonging to the A irreducible representation, and the first six low-lying states belonging to the B irreducible representation.

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* Corresponding author. E-mail: ancborin@iq.usp.br. Fax: +55−11−3815 5579. Phone: +55−11−3091 3073.

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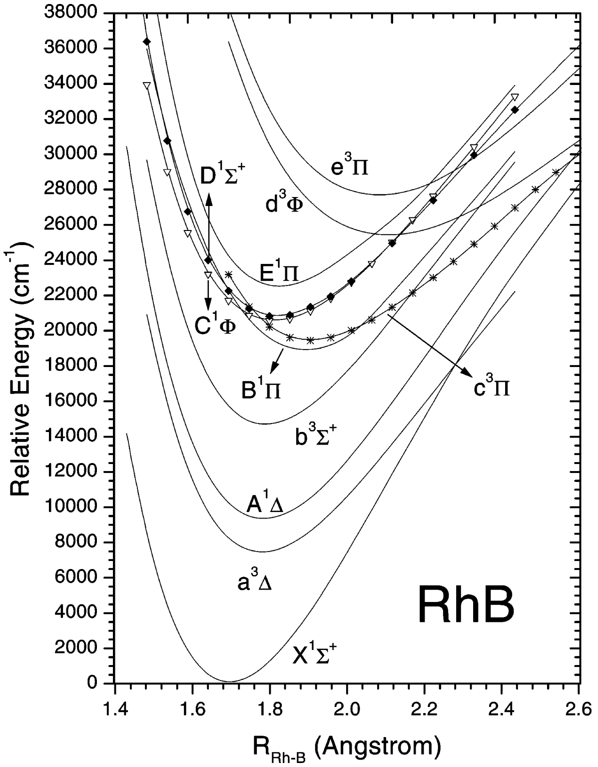

Figure 1. Potential energy curves for the low-lying singlet and triplet electronic states of RhB.

As to the triplets, the three low-lying electronic states belonging to the A irreducible representation plus six other electronic states belonging to the B irreducible representation were included in our calculations. At the CASSCF/MS-CASPT2 level, all electronic states belonging to the same spin and spatial symmetry were taken into account simultaneously. State energies were computed at the MS-CASPT2 level, while state properties were computed using the perturbatively modified CAS-CI (PMCAS-CI)[18] wave functions, which are built as linear combinations of the CASSCF wave functions with coefficients obtained from the quasidegenerated multistate perturbative treatment. Spin−orbit coupling effects were taken into account by employing the RASSI (restricted active space state interaction) approach,[19] with the MS-CASPT2 energies in the diagonal elements of the spin−orbit Hamiltonian and the corresponding PMCAS-CI wave functions; the 11 $\Lambda - S$ electronic states computed in this work were employed. Potential energy curves (Figure 1) were obtained by fitting cubic splines to the computed energies, from which vibrational wave functions, energies, and spectroscopic constants were computed[8,20−23] (Table 1).

3. Results and Discussion

3.1. RhB Singlet Electronic States. The singlet electronic states correlate with the second atomic dissociation limit, with the boron atom in the ground state ($^2P^\circ$ ($2s^2 2p$)) and Rh atom in the first excited state (^2D ($4d^9$)).

As proposed by Chowdhury and Balfour,[1] and corroborated by us,[8] the RhB ground state is a $X^1\Sigma^+$ state (see Table 1 and Figure 1). The computed equilibrium internuclear distance (R_0) is 1.698 Å and $\Delta G_{1/2} = 922$ cm^{-1}, in agreement with the experimental values:[1] $R_0 = 1.691$ Å and $\Delta G_{1/2} = 920$ cm^{-1}. Its wave function is dominated by a single configuration $(0.92)|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^4\rangle$ (Table 2). The Mulliken population analysis is Rh/B: $5s^{0.15}4d_{\delta}^{4.00}4d_{\sigma}^{1.52}4d_{\pi}^{2.95}/2s^{1.88}2p_{\sigma}^{0.44}2p_{\pi}^{0.96}$, with an atomic distribution in the $X^1\Sigma^+$ state given by Rh, $5s^{0.15}4d^{8.47}$/B, $2s^{1.88}2p^{1.40}$, corresponding to a charge of +0.35e on Rh and a dipole moment of 4.54 D.

TABLE 1: Experimental (in Partentheses) and Theoretical (PMCAS-CI) Spectroscopic Constants for the Low-Lying Singlet and Triplet Electronic States of RhB

state	R_e (Å)	R_0 (Å)	ω_e (cm^{-1})	T_e (cm^{-1})	T_0 (cm^{-1})	$\Delta G_{1/2}$ (cm^{-1})	μ (D)	D_0 (eV)
$X^1\Sigma^+$	1.694	1.698 (1.691)[a]	924			922 (920)[a]	4.54	5.6 (>5.0)[b]
$a^3\Delta$	1.782	1.783	805	7337	7315	789	1.76	4.4
$A^1\Delta$	1.777	1.786	793	9287	9221	792	0.86	4.5
$b^3\Sigma^+$	1.782	1.791	800	14628	14566	794	0.31	3.5
$B^1\Pi$	1.893	1.896	657	18881	18753	685	2.92	3.3
$c^3\Pi$	1.902	1.909	630	19453	19305	620	2.01	2.9
$C^1\Phi$	1.810	1.815	694	20551	20436	689	4.45	3.1
$D^1\Sigma^+$	1.818	1.822 (1.870)[a]	750 (663)[a]	20795	20700 (19984)[a]	712 (628)[a]	0.34	3.0
$E^1\Pi$	1.823	1.828	741	22455	22362 (20110)[b]	727 (710)[b]	4.21	2.8
$d^3\Phi$	2.106	2.111	493	25407	25193	493	1.36	2.2
$e^3\Pi$	2.083	2.087	539	27657	27464	539	1.32	1.9

[a] See ref 1. [b] See ref 2.

TABLE 2: Dominant Configurations for the Low-Lying Electronic States of RhB at the PMCAS-CI Level

state	configuration[a]	leading excitation[b]	effective bond order
$X^1\Sigma^+$	$(0.92)\|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^4\rangle$		2.8
$a^3\Delta$	$(0.94)\|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1\rangle$	$2\delta \rightarrow 12\sigma$	2.3
$A^1\Delta$	$(0.92)\|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1\rangle$	$2\delta \rightarrow 12\sigma$	2.3
$b^3\Sigma^+$	$(0.92)\|...10\sigma^2 11\sigma^1 5\pi^4 2\delta^4 12\sigma^1\rangle$	$11\sigma \rightarrow 12\sigma$	1.8
$B^1\Pi$	$(0.86)\|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^4 12\sigma^1\rangle$	$5\pi \rightarrow 12\sigma$	1.9
$c^3\Pi$	$(0.88)\|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^4 12\sigma^1\rangle +$	$5\pi \rightarrow 12\sigma$	1.8
	$(0.22)\|...10\sigma^2 11\sigma^2 5\pi^2 2\delta^4 12\sigma^1 6\pi^1\rangle$	$5\pi \rightarrow 12\sigma$; $5\pi \rightarrow 6\pi$	
$C^1\Phi$	$(0.90)\|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi^1\rangle$	$2\delta \rightarrow 6\pi$	2.2
$D^1\Sigma^+$	$(0.85)\|...10\sigma^2 11\sigma^1 5\pi^4 2\delta^4 12\sigma^1\rangle$	$11\sigma \rightarrow 12\sigma$	1.5
$E^1\Pi$	$(0.86)\|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi^1\rangle +$	$2\delta \rightarrow 6\pi$	2.0
	$(0.22)\|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^4 12\sigma^1\rangle$	$5\pi \rightarrow 12\sigma$	
$d^3\Phi$	$(0.93)\|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^3 12\sigma^2\rangle$	$2\delta \rightarrow 12\sigma$; $5\pi \rightarrow 12\sigma$	1.4
$e^3\Pi$	$(0.86)\|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^3 12\sigma^2\rangle +$	$5\pi \rightarrow 12\sigma$; $2\delta \rightarrow 12\sigma$	1.4
	$(0.30)\|...10\sigma^2 11\sigma^1 5\pi^3 2\delta^4 12\sigma^2\rangle$	$5\pi \rightarrow 12\sigma$; $11\sigma \rightarrow 12\sigma$	

[a] Total coefficient in parentheses. [b] With respect to the ground state.

To better understand the chemical bond, it is necessary to analyze the most relevant valence molecular orbitals (VMO). The 10σ VMO has a strong contribution from the B 2s atomic orbital, plus a smaller one from the Rh $4d\sigma$, and can be described as a very weakly bonding VMO polarized toward the boron atom. The bonding 11σ VMO is a linear combination of the Rh $4d\sigma$ atomic orbital and a hybrid orbital from the B atom, obtained by the combination of the B 2s and $2p\sigma$ atomic orbitals. The 5π VMO is bonding, obtained from the Rh $4d\pi$ and B $2p\pi$ atomic orbitals, distorted toward the B atom, and the 2δ is a nonbonding VMO centered on Rh, corresponding to the $4d\delta$ atomic orbitals. In addition, it is also necessary to consider the 12σ, 6π, and 13σ VMOs in order to describe fully the valence orbitals involved in the chemical bond. The 12σ VMO is an antibonding orbital, with a large contribution from the Rh 5s atomic orbital; the 6π VMO is the corresponding (antibonding) counterpart of the 5π VMO. Finally, the 13σ VMO is an antibonding linear combination between the Rh $4d\sigma$ and B $2p\sigma$ atomic orbitals.

A traditional description of the chemical bond is based on the number of electrons forming the bond divided by two. In agreement with the qualitative molecular orbital analysis carried out by Chowdhury and Balfour,[1] the bonding between the Rh and the B atoms in the $X^1\Sigma^+$ state can be described as a triple bond, with three normal electron-pair bonds (11σ and 5π VMOs), two pairs of electrons localized on the Rh atom (2δ VMO), plus one pair on the B atom (10σ VMO). This traditional description of the chemical bond neglects the fact that some of the electrons may form only a weak bond, or actually no bond at all (if the occupations of the bonding and corresponding antibonding orbitals are both close to one).[24] A better definition can be obtained by considering the occupation numbers of the bonding and antibonding natural orbitals in a multiconfigurational wave function, by applying the effective bond order (EBO) concept,[24,25] defined as:

$$\mathrm{EBO} = \sum \frac{(b_i - ab_i)}{2}$$

The EBO is based on the occupation numbers of the bonding (b_i) and corresponding antibonding (ab_i) natural orbitals. The EBO is a non-integer number, and one may use the next positive integer value to characterize the multiplicity of the bond. The RhB valence natural molecular orbitals, with their corresponding occupation numbers in the ground state, can be represented as $10\sigma^{1.96}11\sigma^{1.92}5\pi^{3.85}2\delta^{3.99}12\sigma^{0.02}13\sigma^{0.08}6\pi^{0.17}$ (π and δ are degenerate pairs of orbitals, with maximum possible occupations of four electrons) resulting in an EBO of 2.8 (Table 2), which indicates a triple bond in the ground state of RhB, made from three two-electron bonds ($11\sigma^2 5\pi^4$). Note, in particular, the small population of the antibonding (12σ, 13σ, and 6π) orbitals. It should be mentioned that the 10σ and 2δ orbitals were not taken into account because they have a strong atomic character, centered on the B and Rh atoms, respectively, and thus play no significant role in bonding.

The experimental dissociation energy obtained from the vibrational data[2] suggests an energy in excess of 5.0 eV. To estimate the dissociation energy of RhB, we computed the Rh $^4\mathrm{F} \rightarrow {}^2\mathrm{D}$ excitation energy within the supermolecule approach. As we have presented before,[8] the Mulliken population analysis of the wave function computed at 50 Å indicates that the correct atomic states have been obtained. However, the computed excitation energy (0.61 eV) is higher than the experimental value (0.34 eV, *J*-averaged value[9]). The possible sources of errors[8,26] are mainly the results of limitations in the active space and the large spin−orbit coupling in the ground state of the Rh atom. Because of computational limitations, it is not possible to increase the active space or to include all electronic states needed to describe the spin−orbit coupling properly. Therefore, we decided to scale our computed Rh $^4\mathrm{F} \rightarrow {}^2\mathrm{D}$ excitation energy to match the experimental value and used the scaled value to compute the dissociation energy of the $X^1\Sigma^+$ state, as it has been done by other authors,[27] resulting in an estimated value of 5.6 eV. The high bond energy is sufficient to overcome the Rh $^4\mathrm{F} \rightarrow {}^2\mathrm{D}$ valence promotion energy.

The $[9.0]^1\Delta$ electronic state, identified for the first time by us,[8] is the $A^1\Delta$ state of RhB ($T_e = 9287$ cm^{-1}, $T_0 = 9221$ cm^{-1}, $R_e = 1.777$ Å, $R_0 = 1.786$ Å, $\omega_e = 793$, and $\Delta G_{1/2} = 792$ cm^{-1}; see Table 1) with an electronic wave function dominated by a single configuration ($(0.92)|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1\rangle$, Table 2) derived from the ground state by a single excitation from the 2δ to the 12σ VMO ($2\delta \rightarrow 12\sigma$). The Mulliken populations are Rh/B: $5s^{0.73}4d_\delta^{3.00}4d_\sigma^{1.63}4d_\pi^{3.24}/2s^{1.83}2p_\sigma^{0.64}2p_\pi^{0.70}$, corresponding to a charge on the Rh atom of $+0.23$ e ($\mu = 0.86$ D). From the valence natural orbital occupation numbers, $10\sigma^{1.96}$-$11\sigma^{1.94}5\pi^{3.85}2\delta^{3.00}12\sigma^{1.00}13\sigma^{0.07}6\pi^{0.17}$, its EBO is computed to be 2.3 (Table 2), with three normal electron pair bonds ($11\sigma 5\pi$) and a population of 1.24*e* in the antibonding orbitals. The transfer of one electron from a nonbonding to an antibonding orbital weakens the chemical bond. The $A^1\Delta$ state dissociation energy is computed to be $D_0 \approx 4.5$ eV. It is worth mentioning that the results reported by Chowdhury and Balfour[2] suggest the presence of a low-lying electronic state with $\Omega = 2$, attributed by experimentalists to the $A^1\Delta$ predicted by us.[8] Indeed, after taking into account spin−orbit coupling effects around the equilibrium internuclear distance, a $\Omega = 2$ state was found at about (T_e) 9700 cm^{-1} above the ground state, with the main component from the $a^1\Delta$ state. The $X^1\Sigma^+$ state is hardly affected. Therefore, one may conclude that the presence of the $A^1\Delta$ state is responsible for the experimental feature of the electronic spectrum reported by Chowdhury and Balfour.[2]

The next singlet excited-state is the $B^1\Pi$ state (Table 1), located $T_e = 18881$ cm^{-1} ($T_0 = 18753$ cm^{-1}) above the ground state, with $\omega_e = 657$ cm^{-1} and $\Delta G_{1/2} = 685$ cm^{-1}. Around its equilibrium internuclear distance of (R_0) 1.896 Å ($R_e = 1.893$ Å), its wave function is dominated by the configuration $(0.86)|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^4 12\sigma^1\rangle$ (Table 2), derived from the ground state by a single excitation ($5\pi \rightarrow 12\sigma$); this implies a charge transfer from the 5π bonding VMO to the antibonding 12σ VMO. From the natural occupation numbers, $10\sigma^{1.96}$-$11\sigma^{1.91}5\pi^{3.06}2\delta^{3.79}12\sigma^{0.89}13\sigma^{0.05}6\pi^{0.34}$, the EBO is 1.9 (Table 2). The Rh/B: $5s^{0.57}4d_\delta^{3.78}4d_\sigma^{1.65}4d_\pi^{2.62}/2s^{1.79}2p_\sigma^{0.74}2p_\pi^{0.71}$ Mulliken populations indicate an atomic distribution in the $B^1\Pi$ state of Rh $5s^{0.57}4d^{8.05}$/B $2s^{1.79}2p^{1.45}$, which corresponds to a charge of $+0.28$ e on the Rh atom and $\mu = 2.92$ D. Its dissociation energy is computed to be $D_0 \approx 3.3$ eV.

The $C^1\Phi$ state is the next excited singlet state (Table 1), located $T_0 = 20436$ cm^{-1} ($T_e = 20551$ cm^{-1}) above the ground state, with an equilibrium internuclear distance of (R_0) 1.815 Å ($R_e = 1.810$ Å) and $\omega_e = 694$ cm^{-1} ($\Delta G_{1/2} = 689$cm^{-1}). Its wave function is best represented by the configuration $(0.90)|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi^1\rangle$ (Table 2), derived from the ground state by a single excitation from the nonbonding 2δ to the antibonding 6π VMO. The Mulliken populations are Rh/B: $5s^{0.30}4d_\delta^{3.00}4d_\sigma^{1.58}4d_\pi^{3.56}/2s^{1.69}2p_\sigma^{0.37}2p_\pi^{1.34}$ and the atomic distribution corresponds to Rh/B: $5s^{0.30}4d^{8.14}/2s^{1.69}2p^{1.71}$. The computed dipole moment is 4.45 D, with a charge of 0.44 e on Rh. The bonding VMO occupation numbers are $11\sigma^{1.82}5\pi^{3.88}$, with the remaining electrons distributed over the nonbonding ($10\sigma^{1.96}2\delta^{3.0}$) and antibonding orbitals ($12\sigma^{0.17}6\pi^{1.12}13\sigma^{0.04}$), resulting in an EBO of 2.2 (Table 2). The computed dissociation energy (D_0) is $\approx$3.1 eV.

At (T_e) 20795 cm^{-1} above the ground state, we find the $[20.0]^1\Sigma^+$ electronic state of RhB, hereafter referred to as the $D^1\Sigma^+$ state, with $T_0 = 20700$ (19984) cm^{-1}, $R_0 = 1.822$ (1.870) Å and $\Delta G_{1/2} = 712$ (628) cm^{-1} (experimental values in parentheses, see Table 1). According to Chowdhury and Balfour,[1] the $D^1\Sigma^+$ state can arise by a single excitation from the ground state, either from the $11\sigma \rightarrow 12\sigma$ or $5\pi \rightarrow 6\pi$, both leading to a less strongly bound state. Our results suggest that the wave function of the $D^1\Sigma^+$ state is governed by a single electronic configuration, $(0.85)|...10\sigma^2 11\sigma^1 5\pi^4 2\delta^4 12\sigma^1\rangle$ (Table 2), derived from the $X^1\Sigma^+$ state by a single electronic transition from the 11σ to the 12σ VMO ($11\sigma \rightarrow 12\sigma$), with no contribution from the other possible excitation ($5\pi \rightarrow 6\pi$) suggested before.[1] Our results also indicate that the 12σ is an antibonding orbital, rather than nonbonding or weakly bonding.[1] The $D^1\Sigma^+$ state is characterized by the following Mulliken population analysis: Rh/B, $5s^{0.58}4d_\delta^{3.88}4d_\sigma^{1.01}4d_\pi^{3.14}/2s^{1.65}2p_\sigma^{0.62}2p_\pi^{0.80}$; which indicates a charge of $+0.14$ e on the Rh atom and $\mu = 0.34$ D. The natural occupation numbers for the occupied active orbitals are $10\sigma^{1.93}11\sigma^{0.74}5\pi^{3.81}2\delta^{3.89}12\sigma^{1.35}13\sigma^{0.06}6\pi^{0.21}$, resulting in an EBO of 1.5 (Table 2), that is, a double bond. The binding energy is estimated to be $D_0 \approx 3.0$ eV.

The $E^1\Pi$ state found (T_0) 22 362 cm^{-1} ($T_e = 22455$ cm^{-1}; Table 1) above the ground state is the last singlet electronic state considered in this work. Around the equilibrium internuclear distance ($R_0 = 1.828$ Å, $R_e = 1.823$ Å), its wave function is dominated by two configurations ($(0.86)|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 6\pi^1\rangle + (0.22)|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^4 12\sigma^1\rangle$, Table 2), derived from the ground state wave function by the following two single excitations: $2\delta \rightarrow 6\pi$ and $5\pi \rightarrow 12\sigma$. Its dipole moment is 4.21 D, with a charge of 0.34 e on the Rh atom. The Mulliken populations are Rh/B: $5s^{0.39}4d_{\delta}^{3.26}4d_{\sigma}^{1.58}4d_{\pi}^{3.32}/2s^{1.69}2p_{\sigma}^{0.52}2p_{\pi}^{1.10}$, pointing to the following atomic distribution: Rh/B, $5s^{0.39}4d^{8.16}/2s^{1.69}2p^{1.62}$. The natural orbital occupation numbers for the VMO orbitals of the $E^1\Pi$ state are $10\sigma^{1.95}11\sigma^{1.81}5\pi^{3.62}2\delta^{3.25}12\sigma^{0.43}13\sigma^{0.05}6\pi^{0.88}$, resulting in an EBO of 2.0 (Table 2). Once again, there are three normal electron-pair bonds ($11\sigma 5\pi$), but the promotion of electrons from nonbonding to antibonding VMOs ($2\delta \rightarrow 6\pi$) and from bonding to antibonding VMOs ($5\pi \rightarrow 12\sigma$) weakens the chemical bond, with a corresponding increase in the population of the antibonding orbitals (1.36e), relative to the ground state. The $E^1\Pi$ state binding energy (D_0) is estimated to be $\approx$2.8 eV.

The new band system reported by Chowdhury and Balfour[2] with (0,0) at 20 110 cm^{-1}, and interpreted as a $^1\Pi - X^1\Sigma^+$ electronic transition, can be attributed to the $E^1\Pi$ state found by us. As can be seen in Table 1, the theoretical results are in accord with experiment ($T_0 = 22\,363$ (20 110 cm^{-1}) cm^{-1} and $\Delta G_{1/2} = 727$ (710) cm^{-1}, experimental values in parentheses); the equilibrium internuclear distance was not determined experimentally. According to our results (see discussion above), the promotion $2\delta \rightarrow 6\pi$ is responsible for the main contribution to the $E^1\Pi$ state wave function, with a small contribution coming from the excitation $5\pi \rightarrow 12\sigma$. As to the bound strength, the EBO analysis indicates that the $E^1\Pi$ state (EBO = 2.0) is less strongly bound than the $X^1\Sigma^+$ state (EBO = 2.8), in accord with the experimental analysis carried out the Chowdhury and Balfour.[2] There is no other $^1\Pi$ electronic state in this energetic region (see Table 1 and Figure 1).

After taking into account spin−orbit coupling effects, around the equilibrium internuclear distance, a $\Omega = 1$ state is found at about (T_e) 22700 cm^{-1} above the ground state, with the main component derived from the $E^1\Pi$ state, which characterizes it as being a $^1\Pi_1$ state. There is no other $\Omega = 1$ state with a main component from $^1\Pi$ states in this energetic region, which is further evidence to associate the $^1\Pi$ state observed experimentally[2] with the computed $E^1\Pi$ state.

3.2. RhB Triplet Electronic States. The triplet states correlate with the first atomic dissociation channel, that leads to both atoms in their ground atomic state: B ($^2P^\circ$ ($2s^2 2p$)) and Rh (^4F ($4d^8(^3F)5s$)).

A single excitation from the nonbonding 2δ to the antibonding 12σ VMO gives rise to the $a^3\Delta$ state, the lowest triplet excited state dissociating into the ground state atomic channel. Located $T_0 = 7315$ cm^{-1} ($T_e = 7337$ cm^{-1}) above the ground state, with an equilibrium internuclear distance (R_0) of 1.783 Å (R_e = 1.782 Å), $\omega_e = 805$cm^{-1} and $\Delta G_{1/2} = 789$ cm^{-1}, its wave function is dominated by the electronic configuration $(0.94)|...10\sigma^2 11\sigma^2 5\pi^4 2\delta^3 12\sigma^1\rangle$, with the following Mulliken populations: $5s^{0.67}4d_{\delta}^{3.00}4d_{\sigma}^{1.63}4d_{\pi}^{3.26}/2s^{1.88}2p_{\sigma}^{0.66}2p_{\pi}^{0.68}$; the atomic distribution corresponds to Rh $5s^{0.67}4d^{7.89}$/B$2s^{1.88}2p^{1.34}$. The charge on Rh is +0.28 e, with a dipole moment (μ) computed to be 1.76 D. The natural occupation numbers for the VMO are $10\sigma^{1.96}11\sigma^{1.94}5\pi^{3.86}2\delta^{3.00}12\sigma^{1.00}13\sigma^{0.07}6\pi^{0.16}$, from which one obtains an EBO of 2.3, reflecting a weaker chemical bond than that found in the ground state, because of a transfer of one electron from the nonbonding 2δ VMO to the antibonding 12σ VMO, resulting in a population of 1.2e in the antibonding orbitals against 0.27e in the ground state. The $a^3\Delta$ state dissociation energy is computed to be $\approx$4.4 eV.

The third electronic excited state (Table 1) is the $b^3\Sigma^+$ state, located $T_0 = 14\,566$ cm^{-1} ($T_e = 14\,628$ cm^{-1}) above the ground state, with an equilibrium internuclear distance (R_0) of 1.791 Å ($R_e = 1.782$ Å) and $\omega_e = 800$ cm^{-1} ($\Delta G_{1/2} = 794$ cm^{-1}). Its wave function is dominated by the electronic configuration $(0.92)|...10\sigma^2 11\sigma^1 5\pi^4 2\delta^4 12\sigma^1\rangle$, being related to the ground state by a single excitation $11\sigma \rightarrow 12\sigma$, involving the transfer of one electron from a bonding (11σ) to an antibonding orbital (12σ). The Mulliken population is Rh/B: $5s^{0.62}4d_{\delta}^{4.00}4d_{\sigma}^{1.09}4d_{\pi}^{3.02}/2s^{1.54}2p_{\sigma}^{0.63}2p_{\pi}^{0.90}$, with an atomic distribution given by Rh/B: $5s^{0.62}4d^{8.11}/2s^{1.54}2p^{1.53}$. The dipole moment is 0.31 D, with a charge of 0.14 e on Rh. The occupancies of the binding valence molecular orbitals are $11\sigma^{1.02}5\pi^{3.81}$, with the remaining electrons distributed over the nonbonding ($10\sigma^{1.93}2\delta^{4.0}$) and antibonding orbitals ($12\sigma^{0.99}6\pi^{0.20}13\sigma^{0.05}$), resulting in an EBO of 1.8. For the $b^3\Sigma^+$ state, the dissociation energy is $\approx$3.5 eV.

The $c^3\Pi$ state ($R_0 = 1.909$ Å ($R_e = 1.902$ Å) and $\omega_e = 630$ cm^{-1} ($\Delta G_{1/2} = 620$ cm^{-1}), see Table 1) is the next excited triplet state, located $T_0 = 19\,305$ cm^{-1} ($T_e = 19\,453$ cm^{-1}) above the $X^1\Sigma^+$ state. It can be obtained by doubly exciting the ground state wave function ($5\pi \rightarrow 12\sigma$; $5\pi \rightarrow 6\pi$), and is characterized by the wave function $(0.88)|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^4 12\sigma^1\rangle + (0.22)|...10\sigma^2 11\sigma^2 5\pi^2 2\delta^4 12\sigma^1 6\pi^1\rangle$. The atomic charge distribution (Rh/B: $5s^{0.67}4d^{7.94}/2s^{1.85}2p^{1.34}$), with Mulliken populations given by Rh/B: $5s^{0.67}4d_{\delta}^{3.94}4d_{\sigma}^{1.60}4d_{\pi}^{2.40}/2s^{1.85}2p_{\sigma}^{0.72}2p_{\pi}^{0.62}$, results in a dipole moment of 2.01 D and a charge of 0.24 e on the Rh atom. The natural orbital occupation numbers for the VMO orbitals of the $c^3\Pi$ state are $10\sigma^{1.95}11\sigma^{1.91}5\pi^{2.89}2\delta^{3.95}12\sigma^{1.02}13\sigma^{0.08}6\pi^{0.20}$, resulting in an EBO of 1.8. The binding energy is estimated to be $D_0 \approx 2.9$ eV.

The last two triplet electronic states included in this work are the $d^3\Phi$ and $e^3\Pi$ states. The wave function for the $d^3\Phi$ state is dominated by the electronic configuration ($(0.93)|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^3 12\sigma^2\rangle$), derived from the ground state by a double excitation ($2\delta \rightarrow 12\sigma$; $5\pi \rightarrow 12\sigma$); therefore, there is a charge transfer from the 2δ and 5π VMOs to the 12σ antibonding VMO. With an equilibrium internuclear distance of (R_0) 2.111 Å ($R_e = 2.106$ Å), it is computed to be (T_0) 25 193 cm^{-1} (T_e = 25 407 cm^{-1}) above the ground state, with a harmonic frequency of (ω_e) 493 cm^{-1} ($\Delta G_{1/2} = 493$cm^{-1}) and $D_0 \approx 2.2$ eV. On the basis of the occupation numbers of the bonding ($11\sigma^{1.93}5\pi^{2.96}$) and antibonding ($12\sigma^{1.88}6\pi^{0.12}13\sigma^{0.10}$) natural orbitals, its EBO is computed to be 1.4. The Mulliken population analysis (Rh/B: $5s^{1.15}4d_{\delta}^{3.00}4d_{\sigma}^{1.81}4d_{\pi}^{2.80}/2s^{1.80}2p_{\sigma}^{1.04}2p_{\pi}^{0.26}$) indicates a charge of 0.14 e on Rh ($\mu = 1.36$ D), and an atomic charge distribution as follows: Rh/B, $5s^{1.15}4d^{7.61}/2s^{1.80}2p^{1.30}$.

The $e^3\Pi$ state is (T_0) 27 464 cm^{-1} ($T_e = 27\,657$ cm^{-1}) higher in energy than the ground state, with an equilibrium internuclear distance (R_0) of 2.087 Å ($R_e = 2.083$ Å), $\omega_e = 539$ cm^{-1} ($\Delta G_{1/2}$ = 539 cm^{-1}) and binding energy (D_0) of 1.9 eV. Around its equilibrium internuclear distance, the wave function is dominated by the configuration $(0.86)|...10\sigma^2 11\sigma^2 5\pi^3 2\delta^3 12\sigma^2\rangle + (0.30)|...10\sigma^2 11\sigma^1 5\pi^3 2\delta^4 12\sigma^2\rangle$, derived from that of the ground state by exciting one electron from each of the 11σ and 5π bonding and the 2δ nonbonding VMOs to the antibonding12σ. The EBO is 1.4. The occupancies of the bonding valence molecular orbitals can be described as Rh/B: $5s^{1.15}4d_{\delta}^{3.00}4$

$d_{\sigma}^{1.81}4d_{\pi}^{2.80}/2s^{1.80}2p_{\sigma}^{1.04}2p_{\pi}^{0.26}$, attributing a charge of 0.14*e* to the Rh atom, with a computed atomic charge distribution given by Rh/B: $5s^{1.11}4d^{7.62}/2s^{1.78}2p^{1.33}$. The dipole moment is 1.32 D.

4. Conclusions

The low-lying $X^1\Sigma^+$, $a^3\Delta$, $A^1\Delta$, $b^3\Sigma^+$, $B^1\Pi$, $c^3\Pi$, $C^1\Phi$, $D^1\Sigma^+$, $E^1\Pi$, $d^3\Phi$, and $e^3\Pi$ electronic states of RhB have been investigated at the ab initio MS-CASPT2 level with extended atomic basis sets and inclusion of scalar relativistic effects. Among the electronic states described in this work, only the $X^1\Sigma^+$, $D^1\Sigma^+$, and $E^1\Pi$ states have been observed experimentally. Except for the $A^1\Delta$ and $D^1\Sigma^+$ states, which have been described by us previously, the others ($a^3\Delta$, $b^3\Sigma^+$, $B^1\Pi$, $c^3\Pi$, $C^1\Phi$, $E^1\Pi$, $d^3\Phi$, and $e^3\Pi$) are described here for the first time. Potential energy curves, spectroscopic constants, dipole moments, binding energies, and chemical bonding aspects are reported for all states.

The RhB molecule possesses a ground electronic state of $^1\Sigma^+$ symmetry. The excited states can be collected into four sets: (i) the first, ranging from (T_0) 7300 to 9200 cm^{-1} ($a^3\Delta$ and $A^1\Delta$ electronic states); (ii) the second including the $b^3\Sigma^+$ state ($T_0 = 14\,566$ cm^{-1}); (iii) the third ranging between (T_0) 18 700 and 22 400 cm^{-1} ($B^1\Pi$, $c^3\Pi$, $C^1\Phi$, $D^1\Sigma^+$, $E^1\Pi$ electronic states); and (iv) the last one with states higher than 25 000 cm^{-1} ($d^3\Phi$ and $e^3\Pi$ electronic states). The $E^1\Pi$ state is responsible for the $^1\Pi - X^1\Sigma^+$ electronic transition reported by Chowdhury and Balfour recently.

Based on the natural occupation numbers, the most important valence molecular orbitals are: 10σ (essentially the B 2s atomic orbitals), 11σ (a bonding VMO, corresponding to the linear combination of the atomic $4d\sigma$ Rh orbital and a hybrid B $2s2p\sigma$ orbital), 5π (a bonding combination between the Rh $4d\pi$ and the B $2p\pi$ atomic orbitals), 2δ (a nonbonding VMO centered on Rh ($4d\delta$)), 12σ (an antibonding orbital, centered on Rh (5s atomic orbital), the 6π VMO (the corresponding counterpart of the 5π VMO), and the 13σ (an antibonding linear combination between the Rh $4d\sigma$ and the B $2p\sigma$ atomic orbitals).

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