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On the ground and some low-lying excited states of ScB: A multiconfigurational study

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The electronic structure of a series of low-lying excited triplet and quintet states of scandium boride (ScB) was examined using multireference configuration interaction (including Davidson's correction for quadruple excitations) and single-reference coupled cluster (CC) methods with averaged natural orbital (ANO) basis sets. The CC approach was used only for the lowest quintet state. The authors have analyzed eight low-lying triplets $^3\Sigma^-(2)$, $^3\Sigma^+$, $^3\Pi(3)$, and $^3\Delta(2)$ dissociating to $\mathrm{Sc}(^2D)/\mathrm{B}(^2P)$ atoms and eight low-lying quintet states $^5\Sigma^-$, $^5\Sigma^+$, $^5\Pi(2)$, $^5\Phi$, and $^5\Delta(3)$ dissociating to $\mathrm{Sc}(^4F)/\mathrm{B}(^2P)$ atoms. They report the potential energy curves and spectroscopic parameters of ScB obtained with the multireference configuration interaction (MRCI) technique including all singly and doubly excited configurations obtained with the ANO-S basis set. For the two lowest states they obtained also improved ANO-L spectroscopic constants, dipole and quadrupole moments as well as scalar relativistic effects based on the Douglas-Kroll-Hess Hamiltonian. They provide the analysis of the bonding based on Mulliken populations and occupation numbers. Since the two lowest states, $^3\Sigma^-$ and $^5\Sigma^-$, lie energetically very close, their principal goal was to resolve the nature of the ground state of ScB. Their nonrelativistic MRCI(Q) (including Davidson correction) results indicate that the quintet is more stable than the triplet by about 800 cm^{-1}. Inclusion of scalar relativistic effects reduces this difference to about 240 cm^{-1}. The dissociation energies for $^5\Sigma^-$ ScB range from 3.20 to 3.30 eV while those for the $^3\Sigma^-$ range from 1.70 to 1.80 eV. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2741522]

I. INTRODUCTION

The significance of transition metals in material chemistry and catalysis is well known. The examination of the first-row transition metal diatomics is an important step, which can provide valuable information for larger systems.[1] For instance, diatomic binding energies can supply estimates of the bond strengths in more complex cage clusters. Studies of diatomics between the first-row (H–Ne) and transition metal atoms are of special interest because of participation of the *d* shell electrons in the bonding. The presence of *d* electrons in the valence shell usually results in a multitude of low-lying excited states spanning a relatively narrow energy range (1–2 eV).[2] This high density of states is often accompanied by numerous avoided crossings resulting in multiminima on potential energy curves. *Ab initio* calculations of molecular properties of these diatomics are associated with a plethora of computational and methodological difficulties. For instance, the benchmark computational studies of transition metal boride cations that have been published recently[2–5] have shown that these systems require large and flexible basis sets as well as balanced treatment of both nondynamical and dynamical electron correlations. These systems often possess significant quasidegeneracy, exhibit numerous avoided crossings, and require both proper choice of active spaces and state averaging for multiconfigurational calculations.

Data on scandium boride are practically absent. To our knowledge, there is no systematic experimental or computational study of this molecule. The only experimental datum available is the dissociation energy of ScB $D_0(298\ \mathrm{K}) = 2.861 \pm 0.653$ eV obtained from measurements reported by Kondratiev.[6] This particular value seems unreliable since the same source gives exactly the same value and error bars for ScB and TiB. The theoretical paper by Lou *et al.*[7] dealing with hollow-cage transition metal/light atom clusters is only marginally related to ScB. As a by-product of this study, a numerical density functional theory binding energy of

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TABLE I. Total atomic energies (in hartree) and energy splittings of atomic states of B and Sc using the ANO-L basis set.

Method/atom	Boron E	 $^4P(2s2p^2) \leftarrow {}^2P(2s^22p)$	Scandium E	 $^4F(4s3d^2) \leftarrow {}^2D(4s^23d)$
MRCISD	$-24.606\,661\,6$ (^2P) $-24.475\,607\,2$ (^4P)	3.566[a]	$-760.057\,293\,3$ (^2D) $-760.004\,195\,2$ (^4F)	1.445[b]
MRCISD(Q)	$-24.606\,681\,4$ (^2P) $24.475\,615\,0$ (^4P)	3.567[a]	$-760.072\,777\,2$ (^2D) $-760.019\,204\,0$ (^4F)	1.458[b]
U-CCSD[c]	$-24.598\,829\,4$ (^2P) $-24.468\,909\,9_5$ (^4P)	3.535	$-760.040\,865\,0$ (^2D) $-759.986\,646\,4_5$ (^4F)	1.475
U-CCSD(T)[c]	$-24.600\,225\,2$ (^2P) $-24.469\,018\,0$ (^4P)	3.570	$-760.051\,289\,8$ (^2D) $-759.995\,912\,0$ (^4F)	1.507
U-CCSDT[c]	$-24.600\,673\,2$ (^2P) $-24.469\,063\,2$ (^4P)	3.581	$-760.052\,130\,0$ (^2D) $-759.999\,207\,5$ (^4F)	1.440
Expt.		3.579 ± 0.002[d]		1.428[e]

[a] 1 doubly occupied and 26 active orbitals in CI reference space.
[b] 1 frozen, 5 doubly occupied, and 12 active orbitals in CI reference space.
[c] K electrons (boron) and KL electrons (Sc) frozen in coupled cluster calculations.
[d] Reference 32.
[e] Reference 33.

3.07 eV and an equilibrium distance of 2.26 Å ($^3\Sigma^-$) implicitly assumed that the ground state is of triplet symmetry. Higher borides, e.g., ScB_2, are used in industry but were never studied theoretically.

Boldyrev *et al.* have found that diatomics consisting of group III elements prefer high-spin states.[8] Preference for high-spin states in transition metal/first-row atom has also been observed by Kalemos and Mavridis.[2] The principal motivation of this study is to map the potential energy curves for the lowest electronic states (triplets and quintets), to determine the nature of the ground state of ScB, and (where possible) to calculate selected spectroscopic properties. In addition, we report dipole moments and the analysis of the bonding mechanism based on Mulliken populations.

TABLE II. Electronic states of ScB and their leading equilibrium electronic configurations. Core: $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^2 2\pi_y^2$.

State	C_0	Configuration
		Triplet states
$1\,^3\Sigma^-$	0.7	$(7\sigma)^2(8\sigma)^2(3\pi_x)^1(3\pi_y)^1$
$1\,^3\Pi$	−0.8	$(7\sigma)^2(8\sigma)^1(3\pi_x)^1(3\pi_y)^2$
$2\,^3\Sigma^-$	−0.6	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^1(3\bar{\pi}_y)^1$
$1\,^3\Delta$	0.6	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^2-(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_y)^2$
$2\,^3\Pi$	0.5	$(7\sigma)^2(8\sigma)^2(3\pi_y)^1(2\delta_{xy})^1-(7\sigma)^2(8\sigma)^2(1\delta_{x^2-y^2})^1(3\pi_x)^1$
$3\,^3\Pi$	0.4	$(7\sigma)^2(8\sigma)^2(1\delta_{x^2-y^2})^1(3\pi_x)^1-(7\sigma)^2(8\sigma)^2(3\pi_y)^1(2\delta_{xy})^1$
$1\,^3\Sigma^+$	0.7	$(7\sigma)^2(8\sigma)^1(3\pi_x)^1(3\pi_y)^1(2\bar{\delta}_{xy})^1$
$2\,^3\Delta$	−0.6	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_y)^2-(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^2$
		Quintet states
$1\,^5\Sigma^-$	−0.8	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^1(3\pi_y)^1$
$1\,^5\Delta$	-0.9_5	$(7\sigma)^2(8\sigma)^1(1\delta_{x^2-y^2})^1(3\pi_x)^1(3\pi_y)^1$
$1\,^5\Phi$	0.9_5	$(7\sigma)^2(8\sigma)^1(3\pi_x)^1(3\pi_y)^1(4\pi_y)^1$
$1\,^5\Pi$	0.7	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(1\delta_{x^2-y^2})^1(3\pi_x)^1$ $+(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_y)^1(1\delta_{xy})^1$
$2\,^5\Pi$	0.7	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_y)^1(1\delta_{xy})^1$ $-(7\sigma)^2(8\sigma)^1(9\sigma)^1(1\delta_{x^2-y^2})^1(3\pi_x)^1$
$2\,^5\Delta$	0.7	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^1(4\pi_x)^1$ $-(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_y)^1(4\pi_y)^1$
$1\,^5\Sigma^+$	0.8	$(7\sigma)^2(9\sigma)^1(3\pi_x)^1(3\pi_y)^1(1\delta_{xy})^1$
$3\,^5\Delta$	0.7	$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^1(4\pi_x)^1$ $+(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_y)^1(4\pi_y)^1$

II. COMPUTATIONAL DETAILS

All multireference calculations were done with the COLUMBUS (Refs. 9–13) suite of programs. The COLUMBUS-MOLCAS interface was used to include scalar relativistic effects within the Douglas-Kroll-Hess approximation.[14–16] Additional single-reference coupled cluster (CC) calculations were done with the ACES II (Ref. 17) and MOLCAS (Refs. 18 and 19) codes. We have used CC model with single and double excitations (CCSD) perturbatively corrected for the triple excitations[20,21] [CCSD(T)] and also full CC model with single, double, and triple excitations (CCSDT).[22,23]

For the accurate and balanced description of the molecular orbitals of the ground and low-lying excited states through the whole range of bond lengths we have used the state-averaged complete active space self-consistent-field (CASSCF) method, employing equal weights for all states. The active space consisted of ten orbitals and ten electrons. These orbitals correspond to the valence space of scandium ($4s$ and $3d$) and boron ($2s$ and $2p$). The Abelian subgroup C_{2v} of $C_{\infty v}$ has been used in the calculations with the order of irreducible representations as $a_1/b_1/b_2/a_2$. Our choice of active space can be described as DOCC 6/2/2/0 and CAS 5/2/2/1, where DOCC stands for the number doubly of occupied orbitals and CAS for the number of the active space orbitals. In subsequent multirefernece configuration interaction (MRCI) calculations with singly and doubly excited configurations we have used for the definition of the reference wave function 4/1/1/0 frozen core orbitals, 2/1/1/0 doubly occupied orbitals, and 5/2/2/1 active orbitals. Thus,

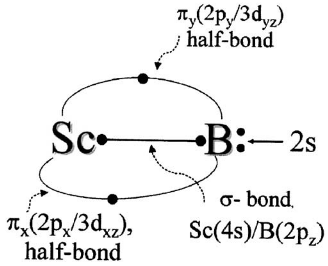

FIG. 1. Lewis structure of the $^3\Sigma^-$ ScB based on MRCI/ANO-L populations and occupation numbers.

there are 7/3/3/1 internal orbitals in our reference and our MRCI calculations include only valence electrons (allowing also the excitations of the $3s^23p^6$ semicore electrons of Sc). This choice is a compromise between desired flexibility of the reference space and computational tractability and leads to more than 71×10^6 configuration state functions (CSFs) for the quintet states and over 166×10^6 CSFs for the triplets.

Two nonrelativistic averaged natural orbital (ANO) basis sets have been used. The smaller one, ANO-S (Pierloot *et al.*[24]), is for Sc($17s12p9d4f$) contracted to [$5s4p3d2f$] and for B($10s6p3d$) contracted to [$4s3p2d$]. The larger one, ANO-L (Widmark *et al.*[25]), is for Sc the [$7s6p5d4f3g$] contraction of the ($21s15p10d6f4g$) primitive set and for B the [$5s4p3d2f$] contraction of the ($14s9p4d3f$) primitive set. For the scalar relativistic calculations the ANO-RCC (Roos *et al.*[26]) basis set contracted to [$7s6p5d4f3g$] and [$5s4p3d2f$] for Sc and B, respectively, has been employed. The resulting orbital space comprises 69 and 151 contracted Gaussian functions, respectively. The ANO-S basis was used for the CASSCF and subsequent multireference configuration interaction calculations with all single and double substitution calculations. Eight triplet and eight quintet states of symmetries Σ, Δ, Π, and Φ were considered in connection with the ANO-S basis. The spectroscopic symbols of the states were assigned according to symmetry representations within the C_{2v} group. Additional resolution was performed on the basis of the computed expectation values of the angular momentum operator $\hat{L}_z$. Since the lowest triplet and quintet states turned out to be very close in energy at the MRCI/ANO-S level, for these two states MRCI calculations with the larger ANO-L and ANO-RCC basis were also performed. For these two states we also calculated spectroscopic constants at the MRCI/ANO-L and MRCI/ANO-RCC levels. Size-extensivity corrections were taken into account by means of the extended Davidson correction and will be denoted as MRCI(Q).[27–29]

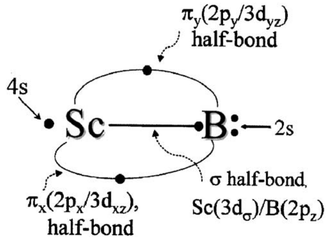

FIG. 2. Lewis structure of the $^5\Sigma^-$ ScB based on MRCI/ANO-L populations and occupation numbers.

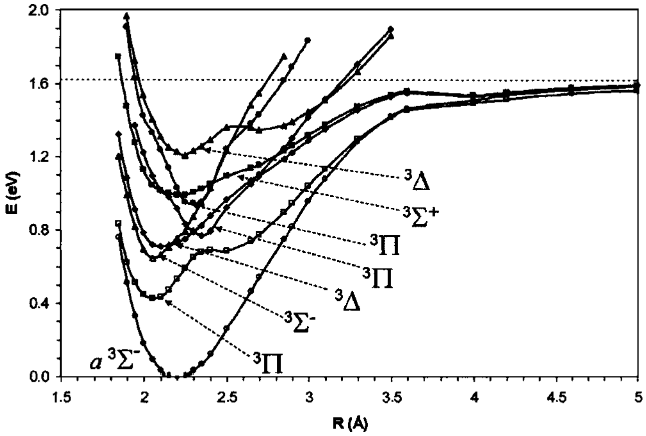

FIG. 3. MRCISD/ANO-S potential energy curves for the triplet states of ScB.

In addition to MRCI, single-reference CCSD(T)/ANO-L and CCSDT/ANO-L calculations were performed for the lowest quintet state of ScB. We could only perform calculations on the $^5\Sigma^-$ state since in this case both CASSCF and MRCI calculations revealed that the dominant configuration was associated with a coefficient of ~0.8, so trying the single-reference CC approach around the minimum seemed to be feasible. Provided that the T_1 and T_2 amplitudes and/or the τ_1 criterion from CC calculations are below a reasonable level, these data should serve as a check for the size-extensivity errors present in the MRCI approach. In CC calculations we have frozen the K (boron) and KL (scandium) inner shells. We report the results of both unrestricted [U-CCSD(T) and U-CCSDT] (Ref. 17) and spin-adapted restricted [R-CCSD(T)] (Refs. 30 and 31) calculations.

Spectroscopic properties, such as the equilibrium distances R_e, the harmonic frequencies ω_e, the anharmonicity corrections $\omega_e x_e$ and α_e, the dissociation energy D_0 (from the vibrational ground state, i.e., $D_0=D_e+\omega_e/2$, where D_e is the minimum on the potential energy curve), and state splittings T_e, are useful for the characterization of the electronic states. For the calculation of the spectroscopic parameters the Dunham analysis and a procedure based on the Morse potential were used. Usually 13-15 points and a seventh to eight order polynomial were used in the fitting and the results from both approaches were identical to the precision given in tables of the next section. Thus, in the next section we present the results of the Dunham analysis.

For the two lowest electronic states we have computed the dipole and quadrupole moments as expectation values (origin was the center of mass).

III. RESULTS AND DISCUSSION

In Table I we present atomic data for energy splittings calculated with various methods and compared with experiment. Electronic states for ScB and their leading configurations are given in Table II. Bonding diagrams for the lowest triplet and quintet states are in Figs. 1 and 2. Potential energy curves obtained from MRCI calculations with the smaller ANO-S basis set are summarized in Figs. 3 and 4. Spectroscopic properties calculated from ANO-S data are presented

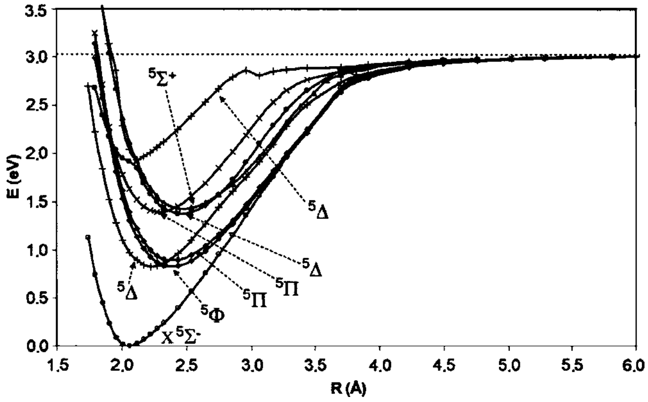

FIG. 4. MRCISD/ANO-S potential energy curves for the quintet states of ScB.

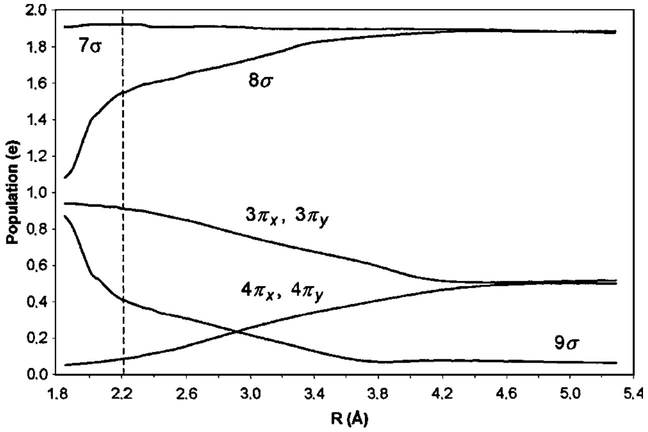

FIG. 5. Evolution of the MRCISD/ANO-L populations of the valence σ and π molecular orbitals of the $^3\Sigma^-$ ScB.

in Table III. MRCI/ANO-L population evolution diagrams of the valence σ and π molecular orbitals of the $X\,^5\Sigma^-$ and $a\,^3\Sigma^-$ states can be found in Figs. 5 and 6, respectively. A summary of MRCI and MRCI(Q) spectroscopic properties and dipole moments computed with the larger ANO-L and ANO-RCC basis sets, respectively, is given in Table IV. The MRCI/ANO-L and MRCI/ANO-RCC dipole moment functions of the $X\,^5\Sigma^-$ and $a\,^3\Sigma^-$ states are displayed in Fig. 7. In both states the polarity of the dipole moments is $\mathrm{Sc}^{\delta+}\mathrm{B}^{\delta-}$.

A. Atomic states

We have calculated the following atomic states for boron: $^2P(2s^22p)$ and $^4P(2s2p^2)$ and for scandium: $^2D(3d4s^2)$ and $^4F(3d^24s)$, the total energies are collected in Table I. This table also compares energy splittings of atomic states computed at different levels of theory with experimental data.[32,33] The agreement between theoretical and experimental doublet/quartet splittings for the B atom is excellent for the MRCI values as well as for U-CCSD(T) and U-CCSDT data. It was possible to choose a quite generous reference space for boron in MRCI (27 internal orbitals in the CI step leading to 752 references for ^2D state and 330 references for ^4F state). In this case, the deviation from the experiment is below 1% for all theoretical values. We stress that spin contamination was negligible in both U-CCSD(T) and U-CCSDT calculations. The comparison between theory and experiment for Sc is also very good. The deviations from experiment lie in the range of 1%–5%, depending on the method. The main source of the deviation from the experiment can be attributed to the treatment of electron correlation, especially proper inclusion of triple excitation contributions in the CC approach. As we can see from the comparison of U-CCSD(T) and U-CCSDT, atomic splitting for Sc is a very sensitive quantity and using just perturbative triples correction is not sufficient. On the other hand, in MRCI higher excitations (besides singles and doubles used here) can only be included by extension of the reference space. Most probably, such limitations in the choice of the active space in MRCI cause the slightly worse agreement with experiment.

TABLE III. MRCI and MRCI(Q) (in parentheses) spectroscopic properties in the ANO-S basis set (distances in Å, energies at equilibrium in hartree, and other data in cm^{-1}).

State	E	R_e	ω_e	$\omega_e x_e$	T_e
$^3\Sigma^-$	−784.592 735 7	2.197	517	4.0	0
	(−784.622 326 8	2.196	484	4.8	0)
$^3\Pi$	−784.576 941 6	2.057	650	12.0	3466
	(−784.608 607 9	2.058	622	7.4	3011)
$^3\Sigma^-$	−784.568 263 6	2.084	655	7.7	5371
	(−784.595 646 7	2.108	648	5.0	5856)
$^5\Sigma^-$	−784.590 162 1	2.073	625	7.8	565
	(−784.623 309 1	2.065	674	7.0	−216)
$^5\Delta$	−784.560 040 8	2.235	534	3.9	7176
	(−784.591 184 5	2.221	531	3.7	6835)
$^5\Phi$	−784.560 063 4	2.393	457	2.5	7171
	(−784.587 069 2	2.382	459	2.8	7738)
$^5\Pi$	−784.557 949 8	2.406	457	2.3	7635
	(−784.584 778 9	2.390	453	2.6	8241)

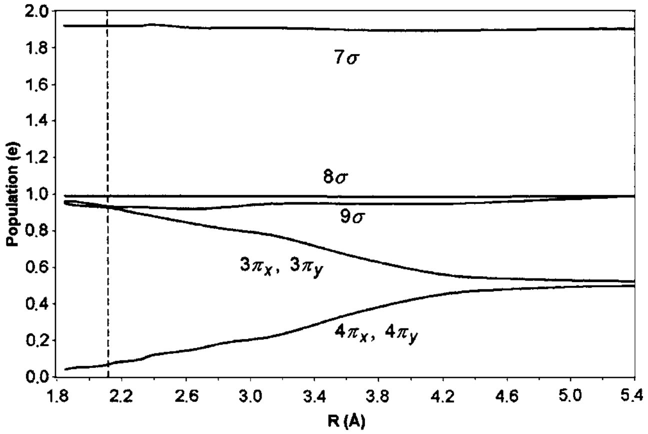

FIG. 6. Evolution of the MRCISD/ANO-L populations of the valence σ and π molecular orbitals of the $^5\Sigma^-$ ScB.

TABLE IV. MRCI, MRCI(Q), and CC properties in the ANO-L basis set (total energies in hartree, distances in Å, dissociation energies in eV, and other data in cm^{-1}). MRCI and MRCI(Q) properties in the ANO-RCC basis set include scalar relativistic corrections.

State	E	R_e	ω_e	$\omega_e x_e$	α_e	T_e	D_0
			MRCISD/ANO-L				
$^3\Sigma^-$	−784.680 003	2.211	493	2.68	0.002	333	1.67
$^5\Sigma^-$	−784.681 567	2.120	600	4.54	0.002	0	3.25
			MRCISD/ANO-RCC				
$^3\Sigma^-$	−788.282 607	2.199	479	3.51	0.004	233	1.40
$^5\Sigma^-$	−788.283 669	2.118	578	3.49	0.003	0	3.50
			MRCISD(Q)/ANO-L				
$^3\Sigma^-$	−784.712 963	2.213	487	3.16	0.002	780	1.79
$^5\Sigma^-$	−784.716 516	2.104	601	3.60	0.003	0	3.30
			MRCISD(Q)/ANO-RCC				
$^3\Sigma^-$	−788.322 250	2.215	484	4.66	0.005	242	1.63
$^5\Sigma^-$	−788.323 353	2.101	596	4.31	0.003	0	3.33
			U-CCSD(T)/ANO-L				
$^5\Sigma^-$	−784.715 323	2.070	674	3.14	0.002	⋯	3.20
			R-CCSD(T)/ANO-L				
$^5\Sigma^-$	−784.714 547	2.068	669	3.31	0.002	⋯	⋯
			U-CCSDT/ANO-L				
$^5\Sigma^-$	−784.719 539	2.098	610	3.67	0.003	⋯	3.22

B. ScB triplets

The bonding in the lowest triplet state $^3\Sigma^-$ is the result of a mixture of four most dominant configurations (data in brackets are corresponding coefficients of the configuration state functions):

$$(7\sigma)^2(8\sigma)^2(3\pi_x)^1(3\pi_y)^1 \quad [0.68],$$

$$(7\sigma)^2(8\sigma)^1(9\bar{\sigma})^1(3\pi_x)^1(3\pi_y)^1 \quad [0.32],$$

$$(7\sigma)^2(9\sigma)^2(3\pi_x)^1(3\pi_y)^1 \quad [-0.27],$$

$$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\bar{\pi}_x)^1(3\pi_y)^1 \quad [-0.22].$$

The analysis of principal contributions to the molecular orbitals 7σ, 8σ, $3\pi_x$, and $3\pi_y$ (and partially also to 9σ) together with corresponding occupation numbers suggests that there is one polarized single σ bond ($7\sigma^2$) and two half-filled π bonds ($3\pi_x^1, 3\pi_y^1$), while the remaining two electrons reside in the nonbonding 8σ orbital with minor weight also in the weakly bonding 9σ orbital. We may represent the bonding situation with the Lewis structure, as depicted in Fig. 1. Alternatively, one can analyze the participation in the bonding in ScB in terms of MRCI Mulliken atomic populations

MRCI

$$\mathrm{Sc}(\sigma)\colon 4s^{0.88}, 4p_z^{0.29}, 3d_\sigma^{0.21}, \quad \mathrm{Sc}(\pi)\colon 3d_{xz}^{0.52}, 3d_{yz}^{0.52},$$

$$\mathrm{B}(\sigma)\colon 2s^{1.83}, 2p_z^{0.73}, \qquad \mathrm{B}(\pi)\colon 2p_x^{0.44}, 2p_y^{0.44}.$$

The evolution of CI electron distribution—NO occupation numbers—with the bond distance for the most important active orbitals 7σ, 8σ, 9σ, $3\pi_x/3\pi_y$, and $4\pi_x/4\pi_y$ is depicted in Fig. 5. The curves in Fig. 5 track the number of electrons in various molecular orbitals (MOs) during the Sc–B bond formation and confirm the transfer of electron density from $4\pi_x/4\pi_y$ with dominating Sc($3d_{xz}/3d_{yz}$) component to $3\pi_x/3\pi_y$ with dominating B($2p_x/2p_y$) component. The occupation numbers of 8σ and 9σ orbitals close to equilibrium distance are in accord with the mixture of four most dominant configurations of the triplet state.

The potential energy curves shown in Fig. 3 belong to states that possess significant multireference character and exhibit complicated patterns including avoided crossings for Π states. The lowest triplet state is separated by ~0.4 eV from the manifold of closely lying excited states that are

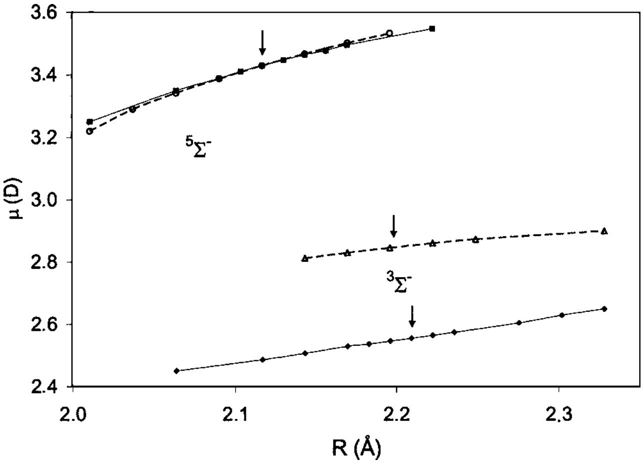

FIG. 7. MRCI/ANO-L (full line) and MRCI/ANO-RCC (dashed line) dipole moment functions of the lowest $^5\Sigma^-$ and $^3\Sigma^-$ states of ScB.

accumulated within an energy range of about 0.8 eV. We have computed the spectroscopic properties (ANO-S basis set) only for the first three triplet states.

The change to the larger ANO-L basis (see Table III) for the lowest $^3\Sigma^-$ state is accompanied by a slight increase in R_e and a slight decrease in ω_e. Together with the calculation at "infinite" distance these data lead to the dissociation energies D_0 of 1.67 eV (MRCI) and 1.79 eV [MRCI(Q)]. MRCISD dipole and quadrupole moments are as follows: μ=2.55 D, $\theta_\perp$=3.95 a.u., and $\theta_\parallel$=−7.89 a.u. The dipole moment function of the $^3\Sigma^-$ state is fairly constant reflecting the cancellation of the opposite changes in occupation numbers of the 8σ and 9σ orbitals at the equilibrium. The impact of relativistic effects on R_e and ω_e is almost negligible, whereas the anharmonicity constants are more sensitive. D_0 is reduced to 1.40 eV (MRCI) and 1.63 eV [MRCI(Q)], respectively. The relativistic shift for MRCI dipole (μ=2.85 D) and quadrupole moments ($\theta_\perp$=3.54 a.u. and $\theta_\parallel$=−7.07 a.u.) is substantial while the shape of the dipole moment function remains unchanged.

We have also checked the possibility to calculate the $^3\Sigma^-$ state at the CCSD(T)/ANO-L level. However, the CCSD calculation at the expected minimum (2.2 Å) showed that both the T_1 and T_2 amplitudes were unacceptably high and we did not continue with CC calculations for the triplet state. This finding confirmed the multireference picture of the $^3\Sigma^-$ state obtained from the CASSCF analysis.

C. ScB quintets

The bonding in the lowest $^5\Sigma^-$ state is a mixture of four most dominant configurations (data in brackets are corresponding coefficients of the configuration state functions):

$$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^1(3\pi_y)^1\ [0.80],$$

$$(7\sigma)^2(8\sigma)^1(9\sigma)^1(4\pi_x)^1(3\pi_y)^1\ [-0.32],$$

$$(7\sigma)^2(8\sigma)^1(9\sigma)^1(3\pi_x)^1(4\pi_y)^1\ [-0.32],$$

$$(7\sigma)^2(8\sigma)^1(11\sigma)^1(3\pi_x)^1(3\pi_y)^1\ [0.28].$$

The analysis of the principal contributions to the CASSCF orbitals 7σ, 8σ, 9σ, 3π, and $3\pi_y$ together with corresponding occupation numbers suggests that there is one lone pair (7σ) located on boron atom, one electron in nonbonding orbital (8σ) located on scandium, a strongly polarized half-filled σ bond (9σ), and two half-filled π bonds. Alternatively, one can present the bonding in ScB in terms of atomic populations at the equilibrium distance

MRCI

$$\mathrm{Sc}(\sigma)\colon 4s^{0.80},4p_2^{0.16},3d_\sigma^{0.60}, \qquad \mathrm{Sc}(\pi)\colon 3d_{xz}^{0.43},3d_{yz}^{0.43},$$

$$\mathrm{B}(\sigma)\colon 2s^{1.75},2p_z^{0.64}, \qquad \mathrm{B}(\pi)\colon 2p_x^{0.54},2p_y^{0.54}.$$

The evolution of the electron distribution—NO occupation numbers—within the most important active orbitals 7σ, 8σ, 9σ, and $3\pi_x/3\pi_y$ and $4\pi_x/4\pi_y$ is depicted in Fig. 6. As expected, the dissociation of the quintet leads to B(^2P) and Sc(^4F) atomic states; however, the detailed analysis showed that above R=4 Å the ground and low-lying excited states are very close to each other. In this region we used the root following technique to resolve the populations in the individual atomic orbitals. There are two groups of states as the system approaches the dissociation limit. In the first group the individual atomic populations within MO 9σ is dominated by the Sc($3d_{z^2}$) orbital (two electrons), while in the second the populations are equally distributed between Sc($3d_{z^2}$) and Sc($4p_z$). This means that it is possible to dissociate either to the Sc($4s3d^2;{}^4F$) or to the Sc($4s4p3d;{}^4F$) atomic states, respectively. Indeed, these scandium atomic states are close in energy,[1] the splitting between them is ~0.5 eV.[33]

Potential energy curves shown in Fig. 4 can be divided into four distinct ranges. The lowest $^5\Sigma^-$ is well separated from the group of next three states ($^5\Phi$, $^5\Delta$, and $^5\Pi$) by ~0.9 eV, while the next group ($^5\Delta$, $^5\Pi$, and $^5\Sigma^+$) is separated by another 0.5 eV. The highest computed state ($^5\Delta$, see avoided crossing between 2.1 and 2.2 Å) lies also 0.5 eV above the third group. The spectroscopic properties (ANO-S) have been computed for the first four quintet states lying within 1 eV range (Table III).

Switching to the larger ANO-L basis for the lowest $^5\Sigma^-$ state (Table IV) results in a small increase in R_e [2.120 Å for MRCI and 2.104 Å for MRCI(Q)] and a slight decrease in ω_e as compared to the smaller ANO-S basis. Together with the calculation at infinite distance the spectroscopic data lead to the dissociation energies of 3.25 eV (MRCI) and 3.30 eV [MRCI(Q)]. MRCI dipole moment and quadrupole moments are as follows: μ=3.43 D, $\theta_\perp$=2.43 a.u., and $\theta_\parallel$=−4.87 a.u. The dipole moment function of the $^5\Sigma^-$ state is fairly constant but exhibits a slightly steeper slope around equilibrium as compared to the $^3\Sigma^-$ state. Scalar relativistic effects for this state turn out to be of minor importance (Table IV). The MRCI multipole moments amount to μ=3.43 D, $\theta_\perp$ =2.48 a.u., and $\theta_\parallel$=−4.95 a.u.

Since the dominant configuration in the CASSCF wave function for the quintet state has a relatively large coefficient (≈0.8) we expected that for this state the CCSD(T)/ANO-L approach could also be feasible around the equilibrium distance. Our CCSD(T) calculations covered the interval of the bond lengths 1.8–2.6 Å and the analysis of CC amplitudes revealed that there are no larger T_2 ones and few acceptably large T_1 ones ($\alpha\alpha$-type excitation, ranging from 0.10 to 0.16). Prompted by is encouraging result and by the fact that for atomic states the full CCSDT approach performed better than CCSD(T) we have also recalculated the potential energy curve at CCSDT/ANO-L level. The resulting spectroscopic constants are in good agreement with MRCI(Q)/ANO-L data and indicate that the size-extensivity error is fairly well removed from MRCI by the Davidson correction.

D. Comparison of triplet and quintet properties

With the ANO-S basis set, the energy difference between the two lowest states, $^3\Sigma^-$ and $^5\Sigma^-$, indicates the triplet as the ground state at the MRCISD/ANO-S level, being by 580 cm^{-1} below the quintet. However, the MRCISD(Q)/ANO-S data favor the quintet as ground state, being

216 cm^{-1} below the triplet, i.e., the ordering is reversed. These triplet/quintet separations are rather small and indicate a quasidegeneracy in ScB and do not allow us to draw a rigorous conclusion about the state ordering. Since the ANO-S basis is far from saturation, the comparison of triplet and quintet states will be based on the ANO-L data.

For both MRCI/ANO-L and MRCI(Q)/ANO-L the quintet is favored. However, the splittings still remain rather small (300–800 cm^{-1}). Including scalar relativistic corrections the energy splitting drops to about 240 cm^{-1}. The two states differ substantially in their spectroscopic properties (Table IV). The equilibrium distance is larger (2.21 Å) and the dipole moment is smaller (2.55 D) for the $^3\Sigma^-$ state as compared to the $^5\Sigma^-$ state (2.10–2.12 Å and substantially larger dipole moment 3.48 D). The difference in dipole moments can be explained comparing the Lewis valence bond structures (Figs. 1 and 2). While in the $^3\Sigma^-$ state there is electron density associated with more diffuse π_x/π_y bonds only weakly polarized, the situation in the $^5\Sigma^-$ state is different. Here, we have polarized π_x/π_y bonds in favor of the boron atom. The distribution of the electron densities associated with the σ bonds is practically the same in both states. There is significant difference between the dissociation energies D_0 of the $^3\Sigma^-$ and $^5\Sigma^-$ states since the potential energy curve for the former state correlates to $\text{Sc}(^2D)/\text{B}(^2P)/$, giving a MRCI(Q)/ANO-L value of $D_0=1.787$ eV. The $^5\Sigma^-$ potential correlates to $\text{B}(^2P)/\text{Sc}(^4F)$, giving $D_0=3.304$ eV at the same computational level. Our vibrational corrections are rather small (less than 0.04 eV); thus, there is no substantial difference between D_0 and D_e. The only experimental datum that can be used for comparison is the dissociation energy reported by Kondratiev[6] and quoted in Ref. 34. Though our value for the quintet state is within the experimental error bars of the experimental dissociation energy (2.86±0.65 eV), we are rather cautious because the reliability of this experimental value is questionable.

IV. CONCLUSIONS

At MRCI/ANO-S level, we have calculated a series of potential energy curves of ScB for two multiplicities—triplets and quintets—and analyzed the electronic structure and the pattern of the manifold of these states. These are the first comprehensive theoretical data reported for scandium boride. We have identified two distinct bonding schemes for $^3\Sigma^-$ and $^5\Sigma^-$ states based on the CASSCF orbitals and MR-CISD population analysis. They differ in the ways how the electron densities (or nonbonding electrons) are distributed among the 8σ and 9σ orbitals along the bond axis.

The two lowest states, $^3\Sigma^-$ and $^5\Sigma^-$, obtained at the MRCI/ANO-L level exhibit significant degree of quasidegeneracy and differ significantly in their dipole moments. However, their energy splitting is rather small (0.03–0.10 eV). Despite this uncertainty, we can tentatively conclude that $^5\Sigma^-$ ScB is the ground state. For the $^5\Sigma^-$ state we computed two sets of spectroscopic constants, first from MRCI(Q) and the second from CCSDT data. We have found very good agreement between both approaches that gives more credibility to the ScB properties calculated in this paper.

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