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G. L. Gutsev
Virginia Commonwealth University

P. Jena
Virginia Commonwealth University

B. K. Rao
Virginia Commonwealth University

S. N. Khanna
Virginia Commonwealth University

Electronic structure and chemical bonding of $3d$-metal dimers ScX, X=Sc–Zn

G. L. Gutsev,[a] P. Jena, B. K. Rao, and S. N. Khanna

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

The electronic and geometrical structures of the ground and excited states of the homonuclear Sc_2, mixed ScTi, ScV, ScCr, ScMn, ScFe, ScCo, ScNi, ScCu, and ScZn $3d$-metal dimers and their anions have been calculated using the density functional theory with generalized gradient approximation for the exchange-correlation potential. The ground states of the neutral dimers are found to be $^5\Sigma_u^-$ (Sc_2), $^6\Sigma^+$ (ScTi), $^7\Sigma^+$ (ScV), $^4\Sigma^+$ (ScCr), $^3\Sigma^+$ (ScMn), $^2\Delta$ (ScFe), $^1\Sigma^+$ (ScCo), $^2\Sigma^+$ (ScNi), $^3\Delta$(ScCu), and $^4\Sigma^+$ (ScZn). A natural bond analysis reveals an antiferrimagnetic spin coupling in the ground states of ScCr, ScMn, and ScFe. This is due to the electron transfer from Sc to the opposite atom and specific bond formations. While each dimer has a unique chemical bonding pattern, most curious is the localization of two $4s$ electrons at both atomic sites in the ground $^5\Sigma_u^-$ state of Sc_2, which leads to formation of two lone pairs and the bonding scheme: $(3d+3d)_\alpha^3(4s+4s)_\beta^1$. No appreciable sd hybridization is found for the ground states of the ScX dimers except for ScNi. Even though the electron affinities of the ScX dimers are relatively low and do not exceed 1 eV, each ScX$^-$ (except ScCo$^-$) possesses at least two states stable towards detachment of an extra electron. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1373693]

I. INTRODUCTION

Elemental (also named as monoatomic or homonuclear) $3d$-metal dimers have received a considerable attention in theoretical and experimental studies.[1,2] Most recent theoretical papers[3,4] have addressed the applicability of a number of contemporary density-functional theory (DFT) and hybrid DFT methods by means of comparison between computed and experimental properties of the dimers from Sc_2 to Cu_2. It has been shown[3,4] that the results obtained with the use of a generalized gradient approximation for the exchange-correlation functional that consists of Becke's exchange[5] and Perdew–Wangs' correlation[6] (referred to as BPW91) are, generally, in better agreement with the experiment than those obtained with other DFT or hybrid DFT methods.

The ground-state spin multiplicities do change irregularly along the series of $3d$ dimers from Sc_2 to Cu_2, but no reasonable explanation for such a behavior as well as trends in chemical bonding of the dimers seem to have been suggested in the literature. A common practice is to relate[7] properties of the dimers with sd-transfer energies $\Delta_{sd} = E(4s^13d^{n-1}) - E(4s^23d^{n-2})$ of the constituent $3d$ atoms. However, Ti_2, V_2, and Ni_2 have the same ground-state spin multiplicity of three while their Δ_{sd}'s are very different (0.81, 0.25, and -0.03 eV, respectively).[8] A similar disparity is observed for Sc_2 and Co_2, which have quintet ground states.

Formal $D_{\infty h}$ symmetry of nuclei in homonuclear dimers could not be the symmetry of electronic states if the latter are antiferromagnetic, i.e., when local magnetic moments at the nuclei have opposite signs. Therefore, it seems to be reasonable to consider first the trends in formation of ground states for mixed d-metal dimers, for example, ScX (X=Ti–Zn) which have lower symmetry $C_{\infty v}$. Sc atom in its ground state ($[Ar]4s^23d^1$) possesses a single $3d$ electron which could serve as a probe when interacting with $3d$ electrons of other $3d$-metal atoms.

Simultaneous computations of the corresponding negatively charged ScX$^-$ ions would provide[9] an additional confidence in a correct assignment of the ground states of the neutral ScX dimers. Even if there is no theorem proven that the ground state spin multiplicity of an anion differs by ±1 from that of the corresponding neutral parent, no example which violates this relationship has yet been reported.

Among the mixed ScX dimers, theoretical data appear to be available only for the ScNi dimer. Calculations[10] for different spin-multiplicity states of this dimer have been performed by a combined approach in which a complete-active-space self-consistent-field (CASSCF) technique has been used in geometry optimizations followed by total energy re-evaluations using a multireference configuration-interaction approach. The ground state of ScNi was found to be $^2\Sigma^+$.

Experimental data are available for ScCr[11] and ScNi.[12–14] Based on the analysis of electron-spin-resonance (ESR) data, the ground state of ScCr has been predicted to be $^6\Sigma$ and that of ScNi to be $^2\Sigma$. The latter assignment is in agreement with the results of theoretical computations.[10] Resonant two-photon ionization spectroscopy has been applied to a study of jet cooled ScNi.[14] No data seems to be available for the ScX$^-$ anions.

The present work is aimed at a detailed study of mixed $3d$-metal dimers ScX (X=Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) along with their singly charged negative ions using the BPW91 approach. This approach was found to be ca-

[a] Electronic mail: glgutsev@hsc.vcu.edu

pable for a fair reproduction of experimental data such as spectroscopic parameters of 3d-metal dimers,[3,4] 3d-metal monoxides,[15] and dioxides,[16] as well as electron affinities of 3d-metal monoxides and dioxides,[15,16] FeO_3, FeO_4,[17,18] MnO_3, MnO_4,[19,20] and pure metal clusters Fe_2 and Fe_3.[9] In addition, we have performed computations of Sc_2, since this dimer opens the ScX series and a number of experimental[21–27] and theoretical[28–40] data are available for comparison. Besides, the Sc_2^- anion has been calculated[41] by a configuration interaction method with singles and doubles.

In order to get an insight into the nature of chemical bonding in homonuclear and mixed d-metal dimers, we have applied a natural bond orbital (NBO) analysis.[42] Our results obtained for the ScX series are believed to be helpful in understanding general trends in formation of mixed and homonuclear d-metal dimers as well as the nature of their chemical bonding.

II. COMPUTATIONAL DETAILS

Our computations are performed using a usual approach when linear combinations of atomic orbitals centered at dimer atomic sites constitute Kohn–Sham one-electron (or molecular) orbitals. For the atomic orbitals we have used a $[15s11p461f/10s7p4d1f]$ basis due to Wachters[43] and Hay[44] referred as to 6-311+G* in the GAUSSIAN 94 software.[45] Optimizations were performed for each permitted spin multiplicity for both neutral and anionic 3d-metal dimers until further increasing the spin multiplicity would result in a dimer state whose total energy is above the energy of dissociation to the corresponding ground-state atoms. In each case, the geometry optimization was carried out by examining the gradient forces at atomic sites until the maximum force was below 3×10^{-4}.

Kohn and Sham[46] have formulated the DF theory for the ground states. This theory has been extended later[47–49] to excited states comprising the lowest energy states in each particular symmetry (spatial and spin) channel. This is important for justification of the DFT application in the present case because transition metal dimers may possess a number of closely spaced states of various orbital spin and angular momenta, thus making determination of the ground states to be a nontrivial problem.

The operator of the spin momentum is not defined in a conventional density functional theory applied here, where only the densities ρ^α and ρ^β of electrons with α and β spins are available. However, having assumed that the total electron density $\rho(\mathbf{r}) = \rho^\alpha(\mathbf{r}) + \rho^\beta(\mathbf{r})$ corresponds to some wave function Ψ satisfying conditions $\hat{S}^2 \Psi = (S+1)S\Psi$ and $\hat{S}_z \Psi = S\Psi$, one can relate the spin multiplicity $M = 2S+1$ and the number of electrons in the spin-up (n_α) and spin-down (n_β) representations as

$$2S+1 = \int [\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})]d\mathbf{r} = n_\alpha - n_\beta + 1. \tag{1}$$

Spatial symmetry of an electronic state obtained from optimizations with a fixed number of "spin-up" (α, majority) and "spin-down" (β, minority) electrons is defined by a direct product of symmetries of partially occupied Kohn–Sham molecular orbitals (MOs) as in conventional Hartree–Fock theory.

The orbital and spin angular momenta each have a magnetic moment associated with them,[50] and the total magnetic moment may be defined as $\mu = -\mu_B(\hat{L}+2\hat{S})$,[50] where μ_B is the Bohr magneton. Within the Heisenberg model, one omits the total angular momentum operator $\hat{L}$ and defines $\mu = g\mu_B\hat{S}$, where g is close to the "spin-only" value of 2.

In order to determine spin densities at atoms which are responsible for the local magnetic moments, one can use conventional Mulliken population analysis.[51] However, a recently developed approach called a NBO analysis[52,53] provides a more convenient scheme for partitioning the electronic density of a system into atomic contributions by constructing localized (Lewis) bonding MOs. Inspection of such bonding MOs would allow one to get an insight into the nature of chemical bonding in a transition-metal compound. Advantages of the NBO analysis are following: (i) it is less sensitive than the Mulliken analysis to basis sets used, (ii) it never results in negative charge values in neutral systems, (iii) it describes more reasonably atomic configurations and bonding in ionic compounds.[52]

The NBO analysis is based on the use of special orthonormal sets of orbitals constructed by the method of an "occupancy-weighted symmetric orthogonalization" from an initial $\{\phi_i\}$ MOs. This orthogonalization differs from a conventional symmetric Löwdin's procedure[54] which searches for such a set of orbitals $\{\phi_i^L\}$ that

$$\sum_i \|\phi_i^L - \phi_i\|^2 = \min \tag{2}$$

by using a weighted search for localized orbitals

$$\sum_i w_i \|\phi_i^W - \phi_i\|^2 = \min, \tag{3}$$

where the weighting factor w_i is the occupancy of the orbital ϕ_i

$$w_i = \int \int \phi_i^*(1)\Gamma(1|1')\phi_i(1')d\tau_1 d\tau_1' \tag{4}$$

and $\Gamma(1|1')$ is the one-particle density operator

$$\Gamma(1|1') = N \int \Psi(1,2,...,N)\Psi^*(1',2,...,N)d\tau_2 \cdots d\tau_N. \tag{5}$$

Since no explicit wavefunction corresponding to optimized DFT electronic densities is available, a reasonable choice appears to be the use of Slater determinants built on Kohn–Sham molecular orbitals in Eq. (5) in the same way as in conventional unrestricted Hartree–Fock approximation.

The bond rupture energy of a ScX dimer is computed as the difference in the ground-state total energies of the dimer and its constituent atoms:

$$D_0(\text{ScX}) = E_{\text{tot}}(\text{Sc}) + E_{\text{tot}}(\text{X}) - E_{\text{tot}}(\text{ScX}) \tag{6}$$

neglecting the zero-point vibrational energy of the ScX dimer, which is smaller than 0.05 eV.

TABLE I. Composition of bonding orbitals (BO) and lone pairs (LP) in the ground states of Sc_2 and Sc_2^-. Eigenvalues of molecular orbitals (ϵ_i) are in electron volts.

| $Sc_2, ^5\Sigma_u^-$ | | α spin $Sc(4s^{0.98}3d^{1.48}4p^{0.04})$ | | | | β spin $Sc(4s^{0.49}3d^{0.01})$ | | | | |
| | | Sc_1 | | Sc_2 | | | Sc_1 | | Sc_2 | |
	ϵ_i	$4s\%$	$3d\%$	$4s\%$	$3d\%$	ϵ_i	$4s\%$	$3d\%$	$4s\%$	$3d\%$
LP	−4.77	100	0	0	0					
LP	−4.77	0	0	100	0					
BO	−4.00	1	48	1	48	−5.34	49	0.5	49	0.5
BO	−3.89	0	48	0	48					
BO	−3.89	0	48	0	48					

| $Sc_2^-, ^4\Pi_u$ | | α spin $Sc(4s^{0.97}3d^{1.47}4p^{0.05})$ | | | | β spin $Sc(4s^{0.49}3d^{0.37}4p^{0.14})$ | | | | |
| | | Sc_1 | | Sc_2 | | | Sc_1 | | Sc_2 | |
	ϵ_i	$4s\%$	$3d\%$	$4s\%$	$3d\%$	ϵ_i	$4s\%$	$3d\%$	$4s\%$	$3d\%$
LP	−0.95	100	0	0	0					
LP	−0.95	0	0	100	0					
BO	+0.50	0	47	0	47	−1.84	49.5	0.5	49.5	0.5
BO	+0.75	0	49.5	0	49.5	+1.22	0	37	0	37
BO	+0.88	0	49	0	49					

III. RESULTS AND DISCUSSIONS

A. Sc₂ dimer

An ESR study[26] has predicted the ground state of Sc_2 to be $^5\Sigma$ while resonance Raman spectra of Sc_2 trapped in argon matrices have shown[27] its vibrational constant to be 239.9 cm^{-1}. No experimental data are available for the equilibrium bond length of the dimer. Theoretical predictions of the Sc_2 ground-state symmetry have broadly varied from $^1\Sigma_g^+$ to triplet and quintet states with various spatial symmetries.[28–40] At present, there seems to be a consensus with respect to the ground state symmetry of Sc_2: $^5\Sigma_u^-$. However, different methods provide different equilibrium bond lengths of the dimer in this state. For example, a CASSCF calculation[40] performed using a basis of Slater-type atomic functions (double-zeta + $4p$, $4d$, and two $4f$) has resulted in $R_e = 2.70$ Å,[40] while another CASSCF calculation[32] carried out with the use of a conventional Gaussian-type basis of a rather good quality—$(14s11p6d3f)/[8s7p4d2f]$—has arrived at a value of 2.79 Å. The computed vibrational frequencies differ by 48 cm^{-1}. DFT methods provide more consistent values of R_e within a shorter range, 2.63 ± 0.02 Å.[3,4,39]

Because calculations performed by various methods lead to different ground state electronic configurations of Sc_2, it is interesting to consider the states of Sc_2 of several spin multiplicities at the BPW91 level of theory. According to our computations, at least three states of Sc_2, namely, $^1\Sigma_g^+$ ($R_e = 2.27$ Å, $\omega_e = 287$ cm^{-1}, $T_e = 0.35$ eV), $^3\Sigma_u^-$ ($R_e = 2.61$ Å, $\omega_e = 256$ cm^{-1}, $T_e = 0.18$ eV), and $^7\Delta_g$ ($R_e = 2.50$ Å, $\omega_e = 240$ cm^{-1}, $T_e = 0.49$ eV) are thermodynamically stable, and the spectroscopic parameters of the two latter states are rather close to those of the ground $^5\Sigma_u^-$ state ($R_e = 2.63$ Å, $\omega_e = 241$ cm^{-1}, $T_e = 0.0$ eV). Thus, it is not surprising that

less accurate methods used in earlier studies found any of the earlier states.

Pápai and Castro[39] have obtained larger total energy separations between the $^1\Sigma_g^+$, $^3\Sigma_u^-$, and $^5\Sigma_u^-$ states using the BP86 approach which is similar to the BPW91. This is probably due to the fact that they have used a smaller (63321/5211/41) basis set. Åkeby and Petterson[37] have obtained many more closely spaced states of Sc_2 for singlet, triplet, and quintet spin multiplicities at a CASSCF level; however, their calculations failed to predict $^5\Sigma_u^-$ to be the ground state of Sc_2, and the calculated R_e of 2.51 Å in this state appears to be too short.

Our early calculations[34] performed by an X_α method with a numerical basis have favored $^1\Sigma_g^+$ as the ground state with $R_e = 2.21$ Å and a triple bond. The present NBO analysis confirm Sc_2 to possess a classic triple bond in its $^1\Sigma_g^+$ state, and the effective electronic configurations of Sc atoms in this state are $4s^{0.99}3d^{1.95}4p^{0.07}$. Now a question arises: What kind of bonding is realized in the Sc_2 dimer in its ground $^5\Sigma_u^-$ state? Let us examine the results of the NBO analysis presented in Table I. First, note that the MOs have no appreciable sd mixing. The MOs are almost pure $3d$ or $4s$ ones and may contain a small admixture of $4p$ and higher atomic orbitals. One could also see from Fig. 1 a rather unusual type of chemical bonding in the ground state of Sc_2: There are two lone pairs, each occupied by one electron, which are entirely composed of $4s$ atomic orbitals localized at Sc sites. That is, instead of an energetically unfavorable promotion of two $4s$ electrons which would approximately cost $2\Delta_{sd}(Sc) = 2.86$ eV, the two $4s$ electrons prefer to form lone pairs at the corresponding two atom sites. There are one $4s + 4s$ and three $3d + 3d$ single bonding orbitals. Since a $(4s + 4s)_\beta$ bonding orbital can accommodate only one elec-
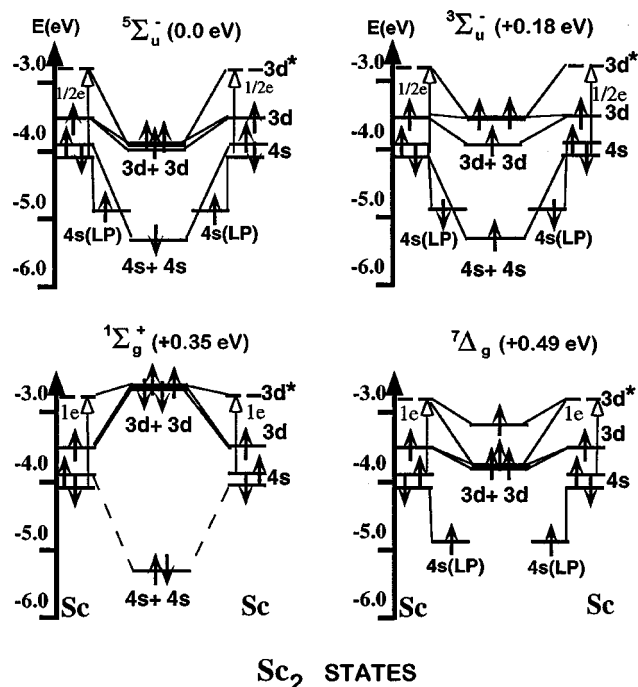
Sc$_2$ STATES

FIG. 1. Bonding patterns in four states of Sc$_2$. $4s$(LP) denotes a lone pair at Sc sites occupied by a single electron. $1/2e$ and $1e$ shows schematically the transfer of $4s$ electrons in $3d*$ manifolds.

tron, another $4s^{\beta}$ electron is promoted to the $3d*$ manifold in order to participate in formation of a $3d+3d$ bonding orbital in the α-spin representation.

Figure 1 presents bonding patterns in all four low-lying states of Sc$_2$. Except the "classically" bonded $^1\Sigma_g^+$ state, all other three states contain $4s$ lone pairs. To indicate a promotion of a single $4s$ electron from both Sc sites, we use an $\frac{1}{2}e$ designation at each site. Atomic energy levels (eigenvalues to the Kohn–Sham equations) are taken from the corresponding atomic computations performed at the same BPW91/6-311+G* level. Formally, all three $^3\Sigma_u^-$, $^5\Sigma_u^-$, and $^7\Delta_g$ states possess four bonding orbitals, but the topmost $^7\Delta_g$ state has no $4s+4s$ bonding orbital. This state is higher in total energy than the $^1\Sigma_g^+$ state by 0.15 eV only, even though the latter has six bonding orbitals. Thus, the number and type of bonding orbitals in a particular electronic state of a $3d$ dimer does not seem to be related directly with the thermodynamic stability of this state.

B. Mixed ScX dimers

The results of our computations for the ScX and ScX$^-$ series are presented in Tables II and III. Following Sc$_2$, ScTi and ScV continue to favor high-spin ground states whose spin multiplicities are six and seven, respectively (see Table II). However, the low spin multiplicity states of ScTi and ScV, which could be considered as following the $^1\Sigma_g^+$ state of Sc$_2$, are rather close in total energy to their ground high spin multiplicity states. ScCr prefers to form a low spin multiplicity ground state $^4\Sigma^+$ which is below its high-spin $^8\Pi$ state by 0.23 eV. ScMn decreases its ground-state spin multiplicity with respect to ScCr by one (see Table II); ScFe and ScCo continue the trend of decreasing ground-state spin mul-

tiplicities. Beginning with ScNi, the spin multiplicity increases to four at ScZn. The anion series shows a similar behavior.

Effective electronic configurations of Sc in the ground-state ScX dimers are rather different. They are close to $4s^{1.5}3d^{1.5}$ in Sc$_2$ and $4s^13d^2$ in ScTi, ScV, and ScZn, while they are closer to $4s^13d^{1.5}$ in ScMn–ScCu. Therefore, one needs additional data in order to understand the peculiarities of the internal structure of various states. The number and content of bonding orbitals and lone pairs appears to be rather helpful in understanding the chemical bonding in the ScX dimers.

First, let us get an insight in the structure of high and low spin multiplicity states of ScTi, ScV, and ScCr. Figure 2 presents the bonding scheme for the two lowest-energy states of ScTi. In both cases, one can see a promotion of $4s$ electrons into the $3d*$ manifolds and formation of a doubly occupied $4s+4s$ orbital. Flipping-up the spins of two electrons occupying the $(3d+3d)_{\beta}$ MOs, which is required formally to obtain the $^6\Sigma^+$ state from the $^2\Sigma^+$ state, does not change the number of bonding orbitals but brings a 0.16 eV gain in total energy.

Compared to ScTi, ScV shows a rather different bonding behavior in both high and low spin multiplicity states (see Fig. 3). Its ground $^7\Sigma^+$ state has a $4s$-lone pair at Sc, a $3d$-lone pair at V, a $4s+4s$ bond and two $3d+3d$ bonds. Note that we preserve the term "lone pair" for a molecular orbital consisting of a localized atomic orbital which is occupied by one electron and the term "bond" for a molecular orbital occupied by two electrons with coupled spins, in order to be consistent with the terminology developed for sp compounds. In this state, a $4s$ electron of V is promoted into a $3d*$ orbital. The $^3\Delta$ state, which is higher in total energy by 0.1 eV, has a $3d$-lone pair at V, while a $4s$ electron of Sc is promoted into an excited $3d*$ orbital of Sc. Formation of an additional $3d+3d$ bonding orbital appears to be not sufficient for compensating the promotional energy at the Sc site.

The high-spin $^8\Pi$ state of ScCr possess two lone pairs ($4s$ and $3d$) at the Sc site and five $3d$ lone pairs at the Cr site (see Fig. 4). It has a $4s+4s$ bond and no $3d+3d$ bonds. The ground $^4\Sigma^+$ state has an interesting bonding scheme which is different from those found previously in the ground states of Sc$_2$, ScTi, and ScV. A $4s$ electron of Sc is partially promoted to an excited $3d*$ orbital at Sc and partially transferred into $3d*$ manifold of Cr in order to form a $(3d+3d)_{\beta}$ bonding orbital. Thus, the formal effective configurations of Sc and Cr are close to $4s^13d^{1.75}$ and $4s^13d^{5.25}$, respectively. There is a double lone $3d$ pair at Cr, two $4s+4s$ bonding orbitals, and five $3d+3d$ bonding orbitals. Note that the formation of five $3d+3d$ bonding orbitals compensates the $4s$ promotion at the Sc site and the $3d$ promotion at the Cr site and provides a 0.23 eV gain in total energy with respect to the promotionless $^8\Pi$ state, which has only one doubly occupied $(4s+4s)$ bonding orbital. As shown in Fig. 5, the ground states of ScMn and ScFe have rather similar chemical bonding patterns. In both of these states, there are $3d$-lone pairs at Mn and Fe sites, and the lowering in the the spin multiplicity when going from ScCr

TABLE II. Equilibrium bond lengths (R_e, in Å), harmonic vibrational frequencies (ω_e, in cm^{-1}), bond dissociation energies (D_0, in eV), dipole moments (DM, in Debye), magnetic moments on atoms (μ_M, in Bohr magneton), effective atomic electronic configurations, and number of bonding orbitals in α and β spin representations (NBO) of the neutral $3d$-metal dimers ScX, X=Sc, Ti, V, Cr, and their anions. ΔE_{tot} (in eV) denote relative positions of the corresponding dimer states.

	Sc$_2$	ScTi		ScV		ScCr	
	$^5\Sigma u-$	$^2\Sigma^+$	$^6\Sigma^+$	$^3\Delta$	$^7\Sigma^+$	$^4\Sigma^+$	$^8\Pi$
	FM	FM	FM	AF	FM	AF	FM
R_e	2.630	2.065	2.290	2.001	2.513	1.990	2.915
ω_e	241[a]	382	272	342	246	262	166
DM	0.0	1.07	0.57	1.54	0.13	1.58	0.43
μ_{Sc}	2.0	0.30	1.50	−0.13	1.50	−0.65	1.60
μ_X	2.0	0.70	3.50	2.13	4.50	3.65	5.40
Sc	$4s^{1.47}3d^{1.48}$	$4s^{0.88}3d^{1.90}$	$4s^{1.17}3d^{1.73}$	$4s^{0.95}3d^{1.80}$	$4s^{1.56}3d^{1.25}$	$4s^{1.02}3d^{1.71}$	$4s^{1.48}3d^{1.36}$
X	$4s^{1.47}3d^{1.48}$	$4s^{1.10}3d^{3.02}$	$4s^{0.81}3d^{3.24}$	$4s^{1.03}3d^{4.18}$	$4s^{1.17}3d^{3.98}$	$4s^{0.98}3d^{5.28}$	$4s^{1.22}3d^{4.88}$
NBO	$3(\alpha)1(\beta)$	$4(\alpha)3(\beta)$	$6(\alpha)1(\beta)$	$4(\alpha)3(\beta)$	$5(\alpha)1(\beta)$	$3(\alpha)3(\beta)$	$1(\alpha)1(\beta)$
ΔE_{tot}	0.0	+0.16	0.0	+0.10	0.0	0.0	+0.23

	Sc$_2^-$	ScTi$^-$		ScV$^-$		ScCr$^-$	
	$^4\Pi g$	$^1\Sigma^+$	$^7\Sigma^+$	$^2\Delta$	$^6\Pi$	$^5\Sigma^+$	$^9\Sigma^+$
	FM	AF	FM	AF	FM	AF	FM
R_e	2.701	2.135	2.368	2.055	2.194	2.039	2.871
ω_e	207	318	237	309	239	223	155
μ_{Sc}	1.5	0.395	2.12	−0.72	0.82	−0.03	1.93
μ_X	1.5	−0.395	3.88	1.72	4.18	4.03	6.07
Sc	$4s^{1.86}3d^{1.52}$	$4s^{1.34}3d^{1.85}$	$4s^{1.66}3d^{1.72}$	$4s^{1.28}3d^{1.78}$	$4s^{1.67}3d^{1.62}$	$4s^{1.57}3d^{1.63}$	$4s^{1.79}3d^{1.90}$
X	$4s^{1.86}3d^{1.52}$	$4s^{1.58}3d^{2.99}$	$4s^{1.28}3d^{3.22}$	$4s^{1.58}3d^{4.16}$	$4s^{1.28}3d^{4.29}$	$4s^{1.33}3d^{5.28}$	$4s^{1.12}3d^{4.93}$
NBO	$3(\alpha)0(\beta)$	$2(\alpha)4(\beta)$	$5(\alpha)1(\beta)$	$4(\alpha)2(\beta)$	$5(\alpha)2(\beta)$	$3(\alpha)3(\beta)$	$0(\alpha)1(\beta)$
ΔE_{tot}	0.0	+0.16	0.0	+0.36	0.0	0.0	+0.44

[a]Experimental $\omega_e=239.9$ (see Ref. 27).

TABLE III. Equilibrium bond lengths (R_e, in Å), harmonic vibrational frequencies (ω_e, in cm^{-1}), bond rupture energies (D_0, in eV), dipole moments (DM, in Debye), magnetic moments on atoms (μ_M, in Bohr magneton), effective atomic electronic configurations, and number of bonding orbitals (NBO) of the neutral $3d$-metal dimers ScX, X=Mn–Zn, along with their anions.

	ScMn		ScFe	ScCo	ScNi[a]	ScCu	ScZn
	$^3\Sigma^+$	$^9\Sigma^+$	$^2\Delta$	$^1\Sigma^+$	$^2\Delta$	$^3\Delta$	$^4\Sigma^+$
	AF[b]	FM[b]	AF	NM	FM	FM	FM
R_e	1.935	2.859	1.849	1.799	2.047	2.497	2.706
ω_e	382	186	474	513	349	215	172
DM	1.74	1.16	2.33	2.65	1.82	1.96	1.37
μ_{Sc}	−1.21	2.35	−0.68	0.0	0.84	1.91	2.66
μ_X	3.21	5.65	1.68	0.0	0.16	0.09	0.34
Sc	$4s^{0.88}3d^{1.69}$	$4s^{1.24}3d^{1.91}$	$4s^{0.90}3d^{1.59}$	$4s^{0.92}3d^{1.50}$	$4s^{1.27}3d^{1.15}$	$4s^{1.14}3d^{1.42}$	$4s^{1.06}3d^{1.94}$
X	$4s^{1.12}3d^{6.25}$	$4s^{1.41}3d^{5.21}$	$4s^{1.10}3d^{7.40}$	$4s^{1.07}3d^{8.28}$	$4s^{1.40}3d^{9.14}$	$4s^{1.49}3d^{9.87}$	$4s^{1.83}3d^{10.00}$
NBO	$4(\alpha)4(\beta)$	$0(\alpha)1(\beta)$	$4(\alpha)5(\beta)$	$4(\alpha)4(\beta)$	$3(\alpha)4(\beta)$	$1(\alpha)1(\beta)$	$0(\alpha)1(\beta)$

	ScMn$^-$		ScFe$^-$	ScCo$^-$	ScNi$^-$	ScCu$^-$	ScZn$^-$
	$^4\Sigma^+$		$^3\Sigma^+$	$^2\Sigma^+$	$^1\Sigma^+$	$^2\Delta$	$^3\Sigma^+$
	AF		FM	FM	NM	FM	FM
R_e	1.997		1.877	1.822	2.095	2.623	2.787
ω_e	279		423	472	317	167	152
μ_{Sc}	−0.41		0.13	0.64	0.0	0.96	1.62
μ_X	3.41		1.87	0.36	0.0	0.04	0.38
Sc	$4s^{1.48}3d^{1.63}$		$4s^{1.42}3d^{1.55}$	$4s^{1.38}3d^{1.48}$	$4s^{1.82}3d^{1.35}$	$4s^{1.82}3d^{1.08}$	$4s^{1.90}3d^{1.76}$
X	$4s^{1.41}3d^{6.25}$		$4s^{1.45}3d^{7.41}$	$4s^{1.48}3d^{8.51}$	$4s^{1.77}3d^{9.17}$	$4s^{1.79}3d^{9.89}$	$4s^{1.92}3d^{10.00}$
NBO	$3(\alpha)4(\beta)$		$3(\alpha)5(\beta)$	$3(\alpha)4(\beta)$	$3(\alpha)3(\beta)$	$0(\alpha)1(\beta)$	$0(\alpha)2(\beta)$

[a]The ground state vibrational interval $\Delta G''_{1/2}$ is 334.5 ± 1.0 cm^{-1} (see Ref. 14).
[b]The ground state is the $^3\Sigma^+$ state and $^9\Sigma^+$ is $+1.45$ eV above.

J. Chem. Phys., Vol. 114, No. 24, 22 June 2001

3 d-metal dimers   10743
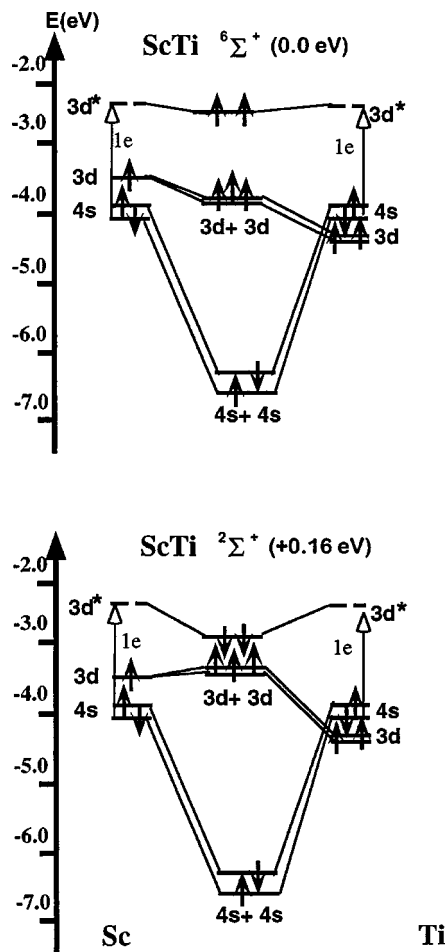

FIG. 2. Bonding patterns in the high and low spin multiplicity states of ScTi.

FIG. 3. Bonding patterns in two states of ScV.

to ScFe is due to increasing the number of $(3d+3d)_\beta$ bonding orbitals.

According to Tables II and III, ScCr, ScMn, and ScFe have antiferromagnetically coupled magnetic moments at nuclear sites. As one could see from Figs. 4 and 5, there is no local magnetic moment related to a lone pair at the Sc sites which is antiferromagnetically coupled to a lone pair at the opposite site. That is, this antiferromagnetic coupling is entirely different from couplings in typical antiferromagnetic 3d-metal dimers such as CrMn.[55] Antiferromagnetic couplings in ScCr, ScMn, and ScFe is due to a partial promotion of a Sc $4s_\alpha$ electron into a $3d^*_\beta$ vacant AOs of Cr, Mn, and Fe.

Electron promotions in ScCo are similar to those in ScCr, ScMn, and ScFe. The ground $^1\Sigma^+$ state of ScCo has one $4s+4s$ bond, three $3d+3d$ bonds, and two double lone pairs at Co. This dimer is thermodynamically most stable in the ScX series (see Table IV). ScNi has the $^2\Delta$ ground state, there is a $4s$-lone pair at Sc and five $3d$-lone pairs at Co, four of which are coupled to each other. This state has a similar bonding pattern as the ground state of ScCo, except a more noticeable mixture of $4s$ and $3d$ orbitals in the bonding MOs.

The bonding pattern in the ground $^3\Delta$ state of ScCu is similar to that in the $^8\Pi$ state of ScCr. The main difference is
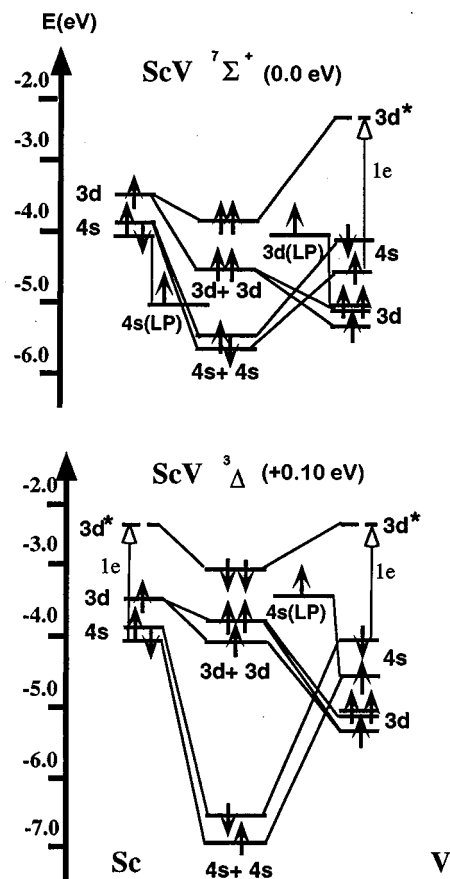
the electron transfer $4s_{Sc} \rightarrow 4s^*_{Cu}$, which is feasible because the latter atomic orbital (AO) is not populated in the ground-state Cu atom. It is shown in Fig. 7 as a half-of-electron transfer from the Sc site to the Cu site. Two lone pairs at Sc are formed in the α spin representation and ten $3d$ electrons of Cu form five coupled $3d$-lone pairs, whose energies are shifted downward with respect to one-electron energy levels of the Cu atom. There is one $4s+4s$ bond with larger contributions from Cu $4s$ AOs. ScZn possesses formally one bonding orbital which can be represented as $0.12 \times 4s_{Sc} + 0.88 \times 4s_{Zn}$. As is seen from Table IV, this bonding is very weak and the dissociation channel ScZn$\rightarrow$Sc+Zn has an energy of 0.16 eV (3.7 kcal/mol) only. Rather, ScZn has to be considered as a van der Waals system.

Attachment of an extra electron increases the population of $4s$ AOs (see Tables II and III), which exceeds the population in reactive states $4s^1 3d^{n-1}$. Since $4s$ states can only form bonding $4s+4s$ and antibonding $4s-4s$ molecular orbitals, it might be anticipated that an antibonding $4s-4s$ MO is filled by an extra electron in the anion states. However, the NBO analysis shows that $4s$ electrons prefer to form lone pairs at both sites. Thus, the gain in total energy is due mainly to lacking promotions of $4s$ electrons into $3d^*$ manifolds. A special case is presented by ScZn$^-$, where $4s$ electrons at both sites are partially promoted into $4p$ AOs. In the lowest $^3\Sigma^+$ state, there is two bonding orbitals: a $(4s + 4s)$ one as in the neutral ground state plus $(4p+4p)$ one.
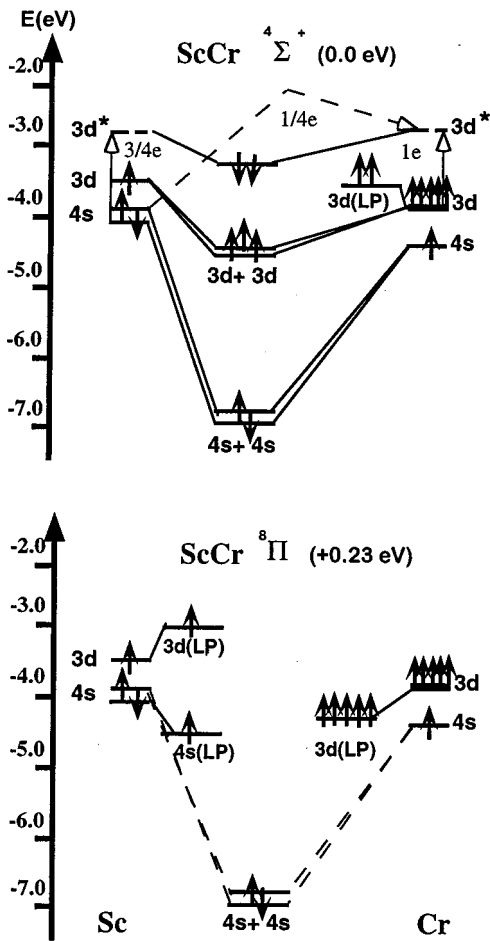
FIG. 4. Bonding patterns in the antiferrimagnetic ($^4\Sigma^+$) and ferrimagnetic ($^8\Pi$) states of ScCr.

FIG. 5. Bonding patterns in the ground (antiferrimagnetic) states of ScMn and ScFe.

Despite the relatively low binding energies of an extra electrons, all the ScX$^-$ anions except ScCo$^-$ possess at least two states which are stable towards detachment of an extra electron. The relative positions of different spin-multiplicity
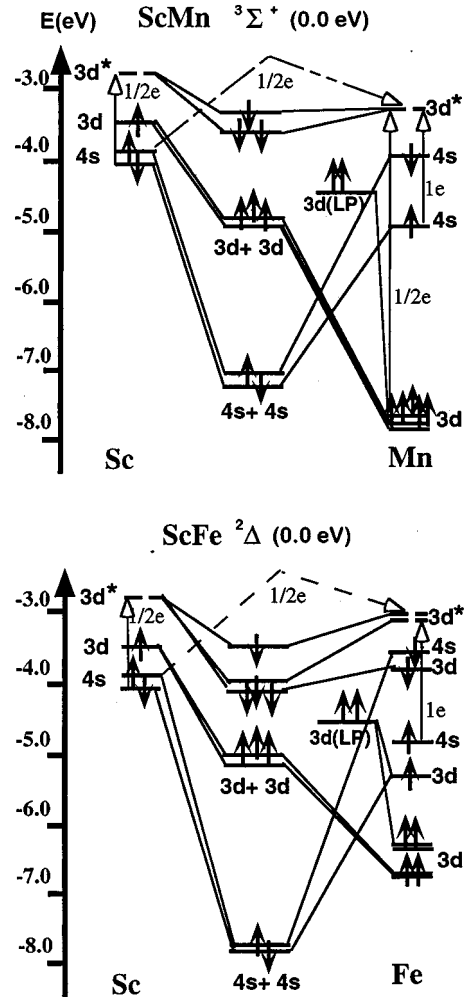
states in the ScX and ScX$^-$ series are presented in Fig. 8. There are plenty of closely spaced states in the beginning of the series, while electron-rich ScFe, ScCo, ScNi, and especially ScCu possess states well separated in total energy.

TABLE IV. Bond rupture energies (D_0), atomic inter-configurational splitting energies $\Delta_{sd}=E(4s^13d^{n-1})-E(4s^23d^{n-2})$, adiabatic electron affinities (A_{ad}), and vertical detachment energies (E_{vd}) for the ground-state ScX dimers, along with experimental atomic intercogfigurational splitting energies $\Delta_{sd}=E(4s^13d^{n-1})-E(4s^23d^{n-2})$, as well as the experimental electron affinities (A) and first ionization potentials (IP) of the constituent ground-state atoms. All values are in electron volts.

	Sc$_2$ $^5\Sigma_u^-$	ScTi $^6\Sigma^+$	ScV $^7\Sigma^+$	ScCr $^4\Sigma^+$	ScMn $^3\Sigma^+$	ScFe $^2\Delta$	ScCo $^1\Sigma^+$	ScNi $^2\Sigma^+$	ScCu $^3\Delta$	ScZn $^4\Sigma^+$
D_0	1.53[a]	2.22	2.57	1.07	1.98	3.19	3.91	3.30	1.74	0.16
$\Delta_{sd}(X)$[b]	1.43	0.81	0.25	−1.00	2.15	0.87	0.42	−0.03	−1.49	⋯
A_{ad}	0.86	0.88	0.74	0.66	0.52	0.51	0.52	0.80	0.86	0.89
$A(X)$[c]	0.18	0.079	0.525	0.666	0.0	0.163	0.661	1.156	1.228	0.0
$E_{vd},M−1$[d]	5.14	5.50	6.18	6.55	6.56	6.86	⋯	5.67	5.72	5.73
$E_{vd},M+1$[d]	5.48	5.36	6.32	6.00	6.20	6.40	6.57	7.21	7.36	8.47
IP(X)[e]	6.56	6.83	6.74	6.77	7.44	7.90	7.86	7.64	7.73	9.39

[a]Experimental $D_0=1.12\pm0.22$ (see Ref. 21), 1.65 ± 0.22 (see Refs. 22–25).
[b]Negative values mean that a $4s^13d^{n-1}$ configuration is the ground state configuration. The lowest excited configuration of Zn is $4s^14p^13d^{10}$.
[c]See Ref. 56.
[d]M is the spin multiplicity of the neutral ground state and $M\mp1$ are the spin multiplicities of the corresponding cations.
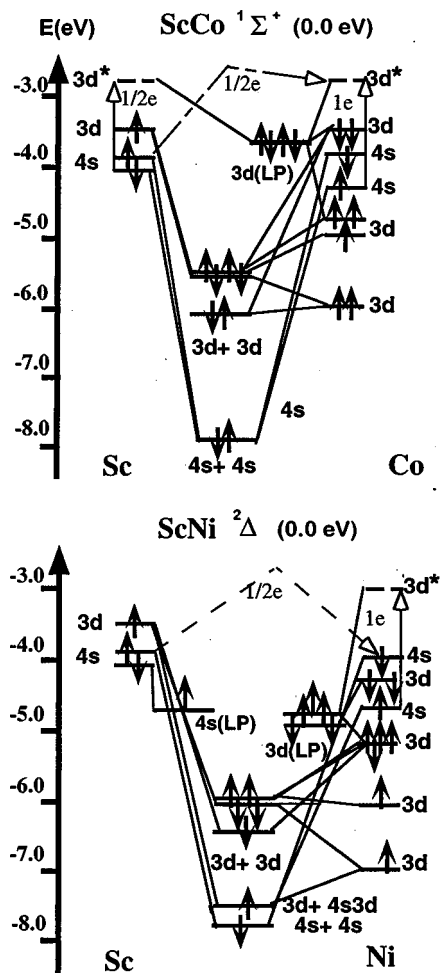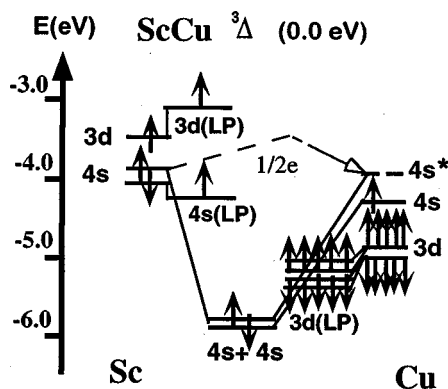[e]See Ref. 8.

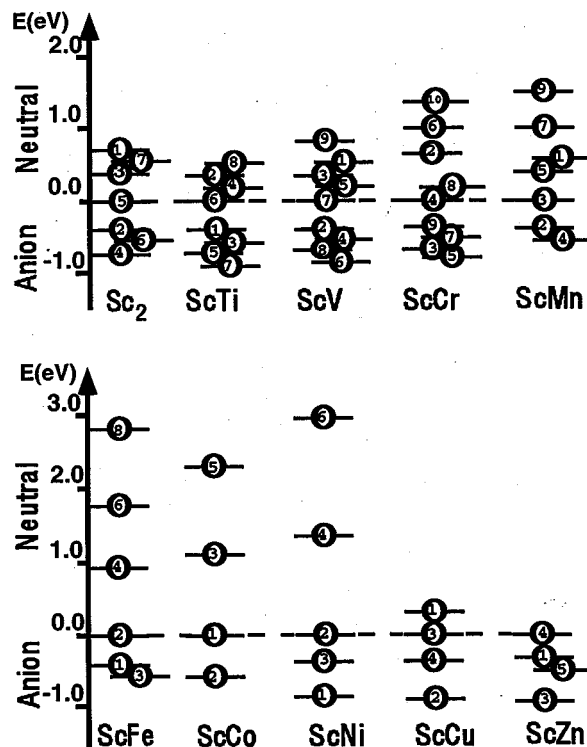FIG. 6. Bonding patterns in the ground states of ScCo and ScNi.

FIG. 8. Relative energies of the excited states of the neutral ScX dimers and their anions given with respect to the total energies of the ground states of each particular neutral dimer. Numbers within the circles denote the spin multiplicity of the corresponding state.

C. Adiabatic electron affinities

The adiabatic electron affinity (A_{ad}) of a neutral dimer is defined as the difference in the ground-state total energies of the dimer and its anion. Within the Born–Oppenheimer approximation, one could evaluate the A_{ad} as

$$A_{ad} = E_{tot}(ScX, R_e) - E_{tot}(ScX^-, R_e^-)$$
$$- \tfrac{1}{2}\omega_e(ScX) + \tfrac{1}{2}\omega_e(ScX^-), \tag{7}$$

FIG. 7. Bonding patterns in the ground state of ScCu.

where R_e and R_e^- denote equilibrium bond lengths of a neutral AB dimer and its AB$^-$ anion, respectively. Since the differences in zero-point vibrational energies, computed within the harmonic approximation, were found to be less than 100 cm^{-1} (0.01 eV), they were neglected.

Our computed values of the A_{ad}s in the ScX series are: Sc$_2$ 0.86 eV, ScTi 0.88 eV, ScV 0.74 eV, ScCr 0.66 eV, ScMn 0.52 eV, ScFe 0.51 eV, ScCo 0.52 eV, ScNi 0.80 eV, ScCu 0.86 eV, and ScZn 0.89 eV. These A_{ad}s have the largest and nearly same values in the beginning and at the end of the series and reach the minimum value of about 0.5 eV at ScMn, ScFe, and ScCo. The estimated full configuration interaction (CI) value[41] of Sc$_2$ is 0.91 eV, which is in agreement with our value of 0.86 eV. Comparison of the dimer A_{ad}s with atomic electron affinities[56] does not show any simple correlation (see Fig. 9).

Experimental electron affinities are available for homonuclear dimers Cr$_2$ (0.505±0.005 eV),[57,58] Fe$_2$ (0.902 ±0.008 eV),[59,60] Co$_2$ (1.110±0.008 eV),[59] and Ni$_2$ (0.926 ±010 eV),[61] as well as the mixed NiCu dimer (0.979 ±0.010 eV).[62] These values have to be compared to our BPW91/6-311+G* results on the A_{ad} computations of the above dimers: Cr$_2$, 0.43 eV;[64] Fe$_2$, 0.94 eV;[9] Co$_2$, 0.91 eV;[63] Ni$_2$, 0.79 eV;[64] and NiCu: 0.85 eV.[64] As is seen, the largest difference between experimental and theoretical values does not exceed 0.2 eV. Such an accuracy has been achieved in A_{ad} computations[65] of typical sp compounds performed by an infinite-order coupled-cluster method with all
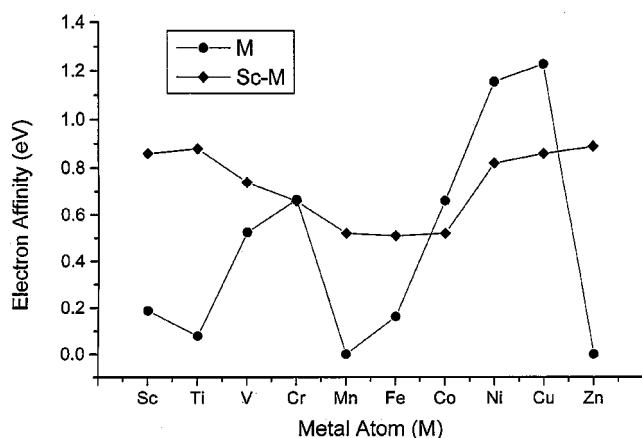
FIG. 9. Comparison of the electron affinities of the ScX dimers and their X constituents.

singles and doubles and noniterative inclusion of triple excitations [CCSD(T) and a 6-311++G($2d,2p$) basis set].

D. Vertical detachment energies

Because detachment of an electron of from a neutral dimer state with the spin multiplicity of M could result in final cationic states with the spin multiplicities of $M \pm 1$, we have computed the vertical detachment energies as

$$E_{vd}, M \pm 1 = E_{tot}(ScX^+, R_e, M \pm 1) - E_{tot}(ScX, R_e, M). \tag{8}$$

Our computed E_{vd}s for the ground state dimers are given in Table IV. As is seen, the vertical detachment energies to high- and low-spin multiplicity states are similar for the dimers from Sc$_2$ to ScFe, while they are splitted at the end of the ScX series. The dimer's E_{vd}s are lower than the lowest detachment energies of an electron [also called the first ionization potentials (FIP)] from the constituent atoms. In fact, only detachment from ScCo$^-$ to the singlet closed-shell ScCo provides the energy of 6.57 eV which matches the Sc FIP of 6.56 eV.

This is rather surprising, because electrons are detached from bonding orbitals. Note that adiabatic detachment energies should be even smaller. In order to get some insight in the nature of such an unusual trend in the E_{vd}s values of the ScX dimers, we have optimized the lowest $^4\Sigma_g^+$ and $^6\Delta_g$ states of Sc$_2^+$ as well as $^5\Delta$ and $^7\Sigma^+$ of ScTi$^+$. Adiabatic detachment energies from the ground $^5\Sigma_u^-$ state of Sc$_2$ are found to be 5.13 and 5.37 eV, which are indeed somewhat lower than the E_{vd}s of 5.14 and 5.48 eV, respectively (see Table IV). Our value of 5.13 eV for the adiabatic detachment energy of an electron in Sc$_2$ is in fair agreement with the value of 4.82 eV obtained at the CI level.[41]

According to the data of the NBO analysis, effective electronic configurations of Sc atoms in the $^4\Sigma_g^+$ (R_e = 2.57 Å, ω_e = 268 cm^{-1}) and $^6\Delta_g$ (R_e = 2.42 Å, ω_e = 270 cm^{-1}) states of Sc$_2^+$ are $4s^{0.98}3d^{1.48}4p^{0.04}$ and $4s^{0.49}3d^{1.96}4p^{0.05}$, respectively. Both states have no lone pairs; the number of bonding orbitals is 4(α)/1β and 5(α)/0β

in these states, respectively. The bonding pattern in the $^4\Sigma_g^+$ state is similar to that in $^3\Sigma_u^-$ state of Sc$_2$ (see Fig. 1) if two lone pairs are replaced by a $(4s+4s)_\beta$ bonding orbital. To arrive at this state, an electron should be detached from a $(3d+3d)$ MO. However, if to compare the bonding pattern in the $^4\Sigma_g^+$ state (one $4s+4s$ bond and three $3d+3d$ bonding orbitals), one would rather infer that the electron is removed from a combination $4s(LP)+4s(LP)$, while another half of $4s(LP)+4s(LP)$ forms a bonding orbital. The bonding pattern in the $^6\Delta_g$ state [one $(4s+4s)_\alpha$ and four $(3d-3d)_\beta$ bonding orbitals] would be the same as in $^7\Delta_g$ state of Sc$_2$ (see Fig. 1) if consider again that the electron is removed from a combination $4s(LP)+4s(LP)$, while another electron of the combination has filled a bonding orbital. If such an analogy is pertinent, then one could reasonably explain why the E_{vd}s of Sc$_2$ are lower than the FIP of Sc. In both cases, the electron leaves a $4s$-lone pair with a subsequent reconstruction of bonding patterns in the cation.

However, such an explanation is not satisfactory for the next ScTi dimer whose ground state possesses no lone pairs. The optimized $^5\Delta$ (R_e = 2.50 Å, ω_e = 274 cm^{-1}) and $^7\Sigma^+$ (R_e = 2.27 Å, ω_e = 295 cm^{-1}) states of ScTi$^+$ provide the adiabatic electron detachment energies of 5.32 and 5.34 eV, respectively. One can see a slight decrease with respect to the corresponding vertical values of 5.50 and 5.36 eV, respectively (see Table IV). Effective electronic configurations are: Sc [$4s^{0.98}3d^{1.37}4p^{0.03}$] and Ti [$4s^{0.86}3d^{2.73}4p^{0.03}$] in $^5\Delta$; Sc [$4s^{0.46}3d^{1.84}4p^{0.03}$] and Ti [$4s^{0.53}3d^{3.12}4p^{0.04}$] in $^7\Delta$. This indicates that an electron is detached from a $3d+3d$ MO during transition $^6\Sigma^+\rightarrow^5\Delta$, while it is detached from a $4s+4s$ MO in $^6\Sigma^+\rightarrow^7\Delta$. Correspondingly, the number of bonding orbitals is 5(α)/1(β) in the $^5\Delta$ state and 6(α)/0(β) in the $^7\Sigma^+$ state, i.e., by one less than in the ScTi ground state [6(α)/1(β), see Table II]. Both these cationic states have no lone pairs. Thus one could surmise that a relative lowering of total energies in (Sc+X)$^+$ with respect to (Sc+X) could be due to lacking unfavorite promotions in the cation states.

The observation that the molecular ionization energies are less than the ionization energy of either of the constituent atom means that the $3d$-metal dimer cations are more strongly bound than their neutral parents. Computations of dissociation energies show the channel Sc$_2^+$($^4\Sigma_g^+$) $\rightarrow$ Sc+Sc$^+$ to have the energy of 2.55 eV, while the channels ScTi$^+$($^7\Sigma^+$)$\rightarrow$Sc+Ti$^+$ and ScTi$^+$($^7\Sigma^+$)$\rightarrow$Sc$^+$+Ti have the energies of 3.39 and 3.00 eV, respectively. Comparing these values to D_0 values of Sc$_2$ and ScTi given in Table IV, we see that the cations Sc$_2^+$ and ScTi$^+$ are more stable than their neutral parents Sc$_2$ and ScTi, respectively, by about 1 eV.

E. Ground-state spin-multiplicity rules

Our assignment of ground state spin multiplicities of the ScX dimers is consistent with the ''±1 rule,'' which states that the spin multiplicity of a neutral ground state has to differ by ±1 from the ground state spin multiplicity of the corresponding anion, as is seen from the following chart.

Sc_2	ScTi	ScV	ScCr	ScMn	ScFe	ScCo	ScNi	ScCu	ScZn
$^5\Sigma_u^-$	$^6\Sigma^+$	$^7\Sigma^+$	$^4\Sigma^+$	$^3\Sigma^+$	$^2\Delta$	$^1\Sigma^+$	$^2\Sigma^+$	$^3\Delta$	$^4\Sigma^+$
Sc_2^-	ScTi$^-$	ScV$^-$	ScCr$^-$	ScMn$^-$	ScFe$^-$	ScCo$^-$	ScNi$^-$	ScCu$^-$	ScZn$^-$
$^4\Pi_g$	$^7\Sigma^+$	$^6\Pi$	$^5\Sigma^+$	$^4\Sigma^+$	$^3\Sigma^+$	$^2\Sigma^+$	$^1\Sigma^+$	$^2\Delta$	$^3\Sigma^+$

According to a common point of view, the effective electronic configuration of a 3d-metal atom is $4s^13d^{n+1}$ in a dimer, that formally allows the two remaining 4s electrons to form a $(4s+4s)$ bond (or two bonding orbitals in α and β spin representations). Thus, one can costruct anticipated ground state multiplicities of XY dimers in two extreme limits: coupling or decoupling of 3d-electron spins in $X\,4s^13d^{n+1}$ and $Y\,4s^13d^{m+1}$ effective electronic configurations. More formally, one might anticipate that the ground state multiplicity $(2S+1)_{G.S.}$ could be expressed as

$$(2S+1)_{G.S.} = |\mathrm{mod}(n+1) \mp \mathrm{mod}(m+1)| + 1, \qquad (9)$$

where the mod function is defined as $N - Integer\,(N/5) \times 5\,(1 \leqslant N \leqslant 11)$. Note that in Zn-containing dimers, an effective electronic configuration could be considered as $4s^13d^{10}4p^1$.

Let us check if this rule works in the ScX series. Sc has a $4s^23d^1$ configuration, thus the Sc_2 dimer should have the ground state spin multiplicity of 1 or 5 in dependence how spins of 3d electrons of two effective electronic configurations $4s^13d^2$ are coupled, i.e., $2S+1=1$ or 5. Indeed, the ground state spin multiplicity is 5. Let us consider the other ScX dimers.

(1) ScTi:Sc($4s^13d^2$)+Ti($4s^13d^3$) should result in $2S+1$ $= 2$ or 6. The ground state has 6.
(2) ScV:Sc($4s^13d^2$)+V($4s^13d^4$) should result in $2S+1$ $= 3$ or 7. The ground state has 7.
(3) ScCr:Sc($4s^13d^2$)+Cr($4s^13d^5$) should result in $2S+1$ $= 4$ or 8. The ground state has 4.
(4) ScMn:Sc($4s^13d^2$)+Mn($4s^13d^6$) should result in $2S+1=3$ or 7. The ground state has 3.
(5) ScFe:Sc($4s^13d^2$)+Fe($4s^13d^7$) should result in $2S+1$ $= 2$ or 6. The ground state has 2.
(6) ScCo:Sc($4s^13d^2$)+Co($4s^13d^8$) should result in $2S+1$ $= 1$ or 5. The ground state has 1.
(7) ScNi:Sc($4s^13d^2$)+Ni($4s^13d^9$) should result in $2S+1$ $= 2$ or 4. The ground state has 2.
(8) ScCu:Sc($4s^13d^2$)+Cu($4s^13d^{10}$) should result in $2S+1=3$. The ground state has 3.
(9) ScZn:Sc($4s^13d^2$)+Zn($4s^14p^13d^{10}$) should result in $2S+1=2$ or 4. The ground state has 4.

The rule (9) for determining the ground state spin multiplicity of a homonuclear or mixed d-metal dimer is so simple, that it hardly believable that is valid for all the d-metal dimers. Indeed, the ground-state spin multiplicities of Ti_2 and V_2 should be 1 or 7 and 1 or 9, respectively, according to this rule. However, the ground spin multiplicity of the both dimers equals three which is in agreement with rule (9) predictions for isoelectronic ScV and ScMn. None the less, such violations are occasional and this simple rule could be very useful when guessing the ground state spin multiplicities of transition metal dimers.

IV. SUMMARY

The results of our density functional theory computations of Sc_2 and Sc_2^- compare well with the results obtained for Sc_2 and Sc_2^- at most advanced levels of theory and experimental data. Our computed vibrational frequencies of Sc_2 and ScNi, 241 and 349 cm^{-1}, respectively, are in good agreement with experimental values of 239.9 cm^{-1} and 334 ± 1.0 cm^{-1}, respectively, that allows one to anticipate a similar accuracy for other mixed dimers ScX.

This first systematic investigation on the electronic structure and chemical bonding of the 3d-metal ScX and ScX$^-$ dimers (X=Sc–Zn) has revealed a number of interesting features.

(i) Each dimer has a specific bonding pattern which is guided by different promotion schemes inside electronic configurations of the constituent atoms.
(ii) Local magnetic moments are coupled antiferrimagnetically in the ScCr, ScMn, and ScFe dimers.
(iii) The ground state multiplicity of a ScX dimer is described by a simple relation (9) between the number of 3d electrons in effective electronic configurations of the constituent atoms.
(iv) Even though the electron affinities of the ScX dimers are within a narrow range ($0.5\,\mathrm{eV} < A_{ad} < 0.9\,\mathrm{eV}$), each dimer except closed-shell ScCo possesses at least two states stable towards detachment of an extra electron. In particular, ScTi$^-$, ScV$^-$, and ScCr$^-$ possess at least four stable states.
(v) The 3d-electron poor dimers Sc_2, ScTi, ScV, ScCr, and ScMn possess several states of different spin multiplicities which are close in total energy to the corresponding ground states, while excited states of the 3d-electron rich dimers ScFe, ScCo, ScNi are well separated in total energy from their ground states.
(vi) Vertical electron detachment energies for a ground-state ScX dimer are smaller than detachment energies of an electron in the ground-state Sc and X atoms.

ACKNOWLEDGMENT

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10748   J. Chem. Phys., Vol. 114, No. 24, 22 June 2001

Gutsev *et al.*

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