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Electronic and Geometric Structures of Several States of Diatomic Scandium Nitride

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Abstract: The electronic and geometric structures of 15 scandium nitride species with formal σ,π,π triple, σ,π double π,π double, σ single, and π single two-electron bonds have been studied by ab initio MCSCF and multireference CI techniques. All 15 species are bound relative to the ground-state atoms. Although Sc has a ^2D $4s^23d^1$ ground state, the ground-state ScN is the triply bonded $^1\Sigma^+$ with a $3d^3$ configuration dominant in situ. The π,π doubly bonded $^3\Sigma^+$ and the σ,π doubly bonded $^3\Pi$ are only 7.4 and 12.1 kcal/mol higher in energy, respectively. Thus, we expect that the σ bond in the triply bonded species will readily be broken by singly bonded R–R′ species resulting in species with a linear RScNR′ framework with π,π doubly bonded Sc–N and σ singly bonded Sc–R and N–R′. Indeed, our MCSCF calculations suggest that linear $^1\Sigma^+$ HScNH is at least 53.6 kcal/mol more stable than ground-state ScN and H_2. A Mulliken population analysis suggests the following: there is a substantial ionic character in these bonds; regardless of the number of formal covalent bonds between N and Sc, the gross Sc to N charge transfer is relatively constant for the 14 species with an in situ $4s^13d^2$, $4s^13d^14p^1$, or $3d^3$ excited-state Sc configuration dominant at equilibrium and is smaller for the one state with an in situ $4s^23d^1$. The term symbol, calculated bond length (R_{eq}, Å), vibrational frequency (ω_e, cm^{-1}), gross Sc to N charge transfer, the absolute bond energy relative to the ground-state fragments (D_e, kcal/mol), and the dipole moment (μ, Debye, with polarity Sc^+N^-) are as follows: Triply bonded species: $^1\Sigma^+$, 1.768, 726, 0.59, 62.7, 5.34. σ,π-Doubly bonded species: $^3\Pi$, 1.839, 802, 0.62, 50.6, 3.79; $^1\Pi$, 1.845, 789, 0.62, 49.8, 3.56; $^3B_1$, 2.061, 566, 0.60, 17.8, 2.23. π,π Doubly bonded species: $^3\Sigma^+$, 1.769, 861, 0.56, 55.3, 2.46; $^3\Delta$, 1.830, 790, 0.63, 11.7, 9.38; $^1\Delta$, 1.843, 785, 0.62, 10.5, 9.22. σ Singly bonded species: $^3\Sigma^-$, 2.058, 577, 0.48, 27.3, 1.75; $^5\Sigma^-$, 2.250, 400, 0.60, 5.6, 2.36; $^5\Pi$, 2.231, 438, 0.64, 10.3, 3.78; $^5\Delta$, 2.173, 489, 0.65, 21.1, 3.67; $^3\Delta$, 2.178, 491, 0.66, 18.9, 3.59; $^1\Delta$, 2.179, 496, 0.67, 17.3, 3.62. π Singly bonded species: $^5\Sigma^+$, 2.102, 530, 0.58, 2.4, 2.26; $^5B_1$, 2.059, 576, 0.60, 13.7, 2.34. The structure of the calculations that we have been using for transition-metal-containing species is discussed with an emphasis on the effect of the interatomic spin couplings on the electronic structures.

I. Introduction

Our current focus[1,2] is the development of a qualitative understanding of the nature of the chemical bonds between a transition element and molecules composed of main-group elements.[1-3] Here we investigate various states of neutral ScN with formal two-electron single, double, and triple bonds. The emphasis will be on describing the multitude of ScN states, including those with multiple bonds, at a uniform level of accuracy in order to reliably determine relative bond strengths as well as bond lengths, spectroscopic parameters, and the atomic orbital occupations.[4] The bond dissociation energy calculations involve all-electron ab initio wave functions for the ScN molecules and the Sc and N atoms. The basic orbital descriptions (MCSCF wave functions) include the essential physics, i.e., account for the strong intraatomic spin couplings on the transition element and the large $4s^2$–$4p^2$ near-degeneracy of the $4s^23d^1$ ^2D ground-state Sc.[5,6] As in our studies of the bonding of a small ligand to early-transition-metal +1 cations,[2] we have included those configurations and spin couplings at the multiconfiguration self-consistent-field (MCSCF) level so that the system will dissociate to the proper SCF spin states. The MCSCF wave function provides structural correlation of the bonds in a generalized valence bond (GVB) fashion[7] PLUS all possible spin couplings among the valence electrons (both bonding and spectator) consistent with the desired spin state. As noted in earlier publications,[2] our experience is that wave functions constructed in this manner result in molecular asymptotic energies at each theoretical level that are equal to the sum of the energies of the atoms at the corresponding level (i.e, are essentially size consistent[8]). Thus the calculated dissociation energies are meaningful. Also, the MCSCF potential curves follow the CI curves, resulting in similar equilibrium bond lengths. The bare neutral metal atoms have a greater number of low-lying states compared to the +1 metal cations,[9] thus increasing the complexity of the computation. We will follow this computational strategy and in addition, for those states that correlate with the ground-state $4s^23d^1$ ^2D Sc, we will incorporate the $4s^2$–$4p^2$ near-degeneracy effect.[5,6] This will properly order the low-lying states of Sc (See Figure 1). We will not correlate the d electrons in the excited states of Sc at the MCSCF level but will place the burden of describing this order correctly as well as the dynamical correlation energy correction on the CI constructed by forming all single and

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[1] Publications on neutral molecules in this series include: (a) Harrison, J. F. *J. Phys. Chem.* **1983**, *87*, 1312. (b) Harrison, J. F. *J. Phys. Chem.* **1983**, *87*, 1323.

[2] Publications on +1 cations in this series include: (a) Kunze, K. L.; Harrison, J. F. *J. Phys. Chem.* **1989**, *93*, 2983. (b) Alvarado-Swaisgood, A. E.; Allison, J.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 2517. (c) Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1985**, *89*, 5198. (d) Harrison, J. F. *J. Phys. Chem.* **1986**, *90*, 3313. (e) Mavridis, A.; Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1986**, *90*, 2584. (f) Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1988**, *92*, 2757. (g) Alvarado-Swaisgood, A. E.; Harrison, J. F. *J. Phys. Chem.* **1988**, *92*, 5896. (h) Alvarado-Swaisgood, A. E.; Harrison, J. F. *THEOCHEM* **1988**, *46*, 155.

[3] Publications on metal nitride neutral dimers and +1 cations by theoretical groups besides our own include: (a) Jeung, G. H.; Koutecky, J. *J. Chem. Phys.* **1988**, *88*, 3747. (b) Carlson, K. D.; Claydon, C. R.; Moser, C. *J. Chem. Phys.* **1987**, *46*, 4963. (c) Allison, J. N.; Goddard, W. A., III *Chem. Phys.* **1983**, *81*, 263. (d) Panas, I.; Schule, J.; Brandemark, U.; Siegbahn, P. E. M.; Wahlgren, U. *J. Phys. Chem.* **1988**, *92*, 3079. (e) Siegbahn, P. E. M.; Blomberg, M. R. *Chem. Phys.* **1984**, *87*, 189.

[4] Recent publications of the theoretical groups besides our own currently active in calculations on neutral transition-metal–main-group dimers include: (a) Langhoff, S. R.; Bauschlicher, C. W., Jr. *Annu. Rev. Chem.* **1988**, *39*, 181. (b) Langhoff, S. R.; Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1988**, *89*, 396. (c) Langhoff, S. R.; Bauschlicher, C. W., Jr.; Pettersson, L. G. M.; Siegbahn, P. E. M. *Chem. Phys.* **1989**, *132*, 49. (d) Jasien, P. G.; Stevens, W. J. *Chem. Phys. Lett.* **1988**, *147*, 72.

[5] Botch, B. H.; Dunning, T. H., Jr.; Harrison, J. F. *J. Chem. Phys.* **1981**, *75*, 3466.

[6] (a) Bauschlicher, C. W., Jr.; Walsh, S. P. *J. Chem. Phys.* **1982**, *72*, 4560. (b) Walsh, S. P.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1983**, *78*, 4597.

[7] (a) Goddard, W. A., III; Dunning, T. H.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368. (b) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *J. Am. Chem. Soc.* **1972**, *94*, 8293. (c) Bobrowicz, F. W.; Goddard, W. A., III In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4.

[8] Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359, and references therein.

[9] Moore, C. E. *Atomic Energy Levels*; National Standard Reference Data Series; National Bureau, of Standards: Washington DC, 1971; Vol. I and II, Circular 35.

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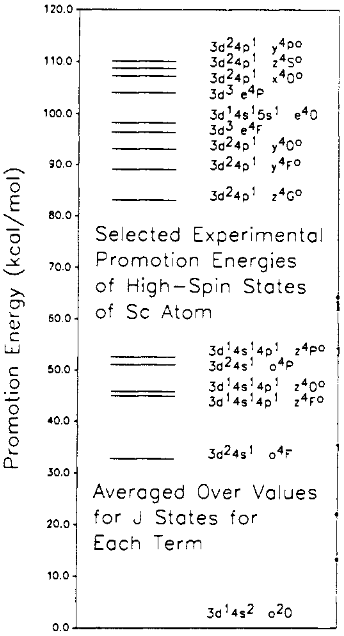


Figure 1. Selected experimental promotion energies of high-spin states of the Sc atom. Reference 9, averaged over values for J states for each term.

double excitations over the MCSCF reference space (MCSCF+1+2).

Several states of the ScN molecule have been studied theoretically by Jeung and Koutecky.[3a] They predicted the ground state of neutral ScN to be a weakly bound singly bonded $^5\Delta$ state with moderate Sc to N charge transfer, a bond energy (D_e) of only 14.1 kcal/mol, and a bond length greater (R_{eq}) than 2.1 Å. They also predicted the second and third most stable states to be $^3\Sigma^-$ and $^5\Pi$, respectively, which are also singly bonded species with comparable energies but slightly shorter bond lengths. By comparison we find the ground state to be a triply bonded $^1\Sigma^+$ state with a D_e with respect to the ground-state atoms of 62.7 kcal/mol and a R_{eq} of 1.768 Å. Previous theoretical studies of nitrides of later transition metals include the triply bonded $^4\Sigma^-$ MoN[3c] (R_{eq} = 1.60 Å, D_e = 93.9 kcal/mol), triply bonded $^2\Delta$ FeN (R_{eq} = 1.667 Å, D_e = 20.8 kcal/mol),[3e] and σ,π doubly bonded $^2\Pi$ NiN (R_{eq} = 1.73 Å, D_e = 35.2 kcal/mol).[3d,e]

To our knowledge there are no experimental results on ScN species. However, since the 1960s when MoN[10a] and NbN[10b] were detected, several gaseous neutral diatomic transition-metal nitrides have been characterized experimentally,[10,11] including TiN, VN, and CrN. Mass spectrometric data indicate that these early-transition-metal nitrides have significant bond energies of 113 (TiN), 113 (VN), and 88 (CrN) kcal/mol, respectively.[11] Rotational analysis of the red electronic emission system of TiN by Dunn et al.[10c] indicates that ground-state $^2\Sigma^+$ TiN has a short bond length of 1.582 Å, similar to the R_{eq} = 1.586 Å we found theoretically[2a] for the triply bonded +1 cation, $^1\Sigma^+$ TiN$^+$. However, earlier theoretical[3b] studies indicated that the TiN bond length was shorter, with R_{eq} = 1.504 Å and D_e = 124 kcal/mol. Likewise, recent spectroscopic work reports bond lengths[10g,10h] for $^3\Delta$ VN of 1.566 and 1.574 Å, respectively, in excellent agreement with our results from triply bonded $^2\Delta$ VN$^+$.

After a preliminary introduction to the molecular species studied, the results on 15 ScN species that we found to be bound with respect to the ground-state atoms are presented and discussed, including the symmetries, bond strengths, bond lengths, spectroscopic properties, and bonding description and the identity of the ground and first excited state. Then predictions of chemistry and the computation of the reaction of the ground-state ScN with H_2 are presented. A discussion of the structure of our computations follows, which describes the atoms and the computational details for a few molecular states as examples. Then general computational details, including the basis sets, molecular codes, and the MCSCF wave function construction for HScNH is described in the Appendix.

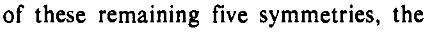
II. Preliminaries

Intention. We are interested in two classes of low-lying states of diatomic scandium nitride, those that dissociate to the ground-state Sc atom and a ground-state N atom and those that separate into a high-spin excited-state Sc atom and a ground-state N atom. There are interesting orbital occupation and spin-coupling options available for the interaction of electrons on Sc with those on N. Our purpose is the determination of the ground state of ScN and the relative bond strengths of various formally $\sigma,\pi\pi$ triply, σ,π doubly, π,π doubly, σ singly, and π singly bonded species. In all, 15 ScN states were studied.

These calculations were carried out in C_{2v} symmetry with the molecular axis, the z axis, as the a_1 symmetry axis and with x and y as b_1 and b_2, respectively. The Sc valence orbital designation and symmetries are as follows: s is 4s (a_1), dσ is 3d$_{z^2}$(a_1), dπ_x is 3d$_{xz}$ (b_1), dπ_y is 3d$_{yz}$ (b_2), δ_+ is 3d$_{x^2-y^2}$ (a_1), and δ_- is 3d$_{xy}$ (a_2). N valence orbital designation and symmetries are as follows: s is 2s (a_1), pσ is 2p$_z$(a_1), p$_x$ is 2p$_x$ (b_1), and p$_y$ is 2p$_y$ (b_2).

Atomic Fragments. The ground state[9] of N is a ^4S associated with the $2s^22p^3$ valence electron configuration. While the ^2D ground state[9] of Sc arises from the configuration (Ar core) $3d^14s^2$, there are many other low-lying excited states. The orders of the excited states associated with the $3d^24s^1$, $4s^13d^14p^1$, $3d^24p^1$, $3d^3$, and $3d^14s^15s^1$ valence electron configurations are interleaved as can be seen in Figure 1, where the relative experimental energies of the relevant high-spin states are displayed with their term symbol and configuration. Notice that the states of Sc with the $3d^24s^1$ and the $4s^13d^14p^1$ configurations have similar energies. These term symbols and experimental promotion energies (kcal/mol)[9] are a^{4}F (32.8) and a^{4}P (51.0) for the $3d^24s^1$ configuration and z^{4}F^0 (45.0), z^{4}D^0 (45.8), and z^{4}P^0 (52.6) for the $4s^13d^14p^1$ configuration. For simplicity we will only discuss Sc in the $3d^24s^1$ configuration. The states of Sc with the $3d^3$, the $3d^24p^1$, and the $3d^14s^15s^1$ configurations also have similar energies, the term symbol and experimental promotion energies[9] being e^{4}F (96.4) and e^{4}P (104.1) for the $3d^3$ configuration, z^{4}G^0 (83.1), y^{4}F^0 (89.1), y^{4}D^0 (93.2) x^{4}D^0 (107.2), z^{4}S^0 (108.8), and y^{4}P^0 (110.) for the $3d^24p^1$ configuration, and e^{4}D(98.3) for the $3d^14s^15s^1$ configuration. Again, for simplicity we will deal only with the $3d^3$ configuration for our discussion. For a given configuration some of the real orbital occupancies used in our calculations correspond to a mixture of the states of that configuration.

States of ScN That Dissociate to the Ground-State ^2D Sc and ^4S N Atoms. The ^2D state of Sc can combine with the ^4S state of N to form ScN states of $^3\Sigma^-$, $^5\Sigma^-$, $^3\Pi$, $^5\Pi$, $^3\Delta$, and $^5\Delta$ symmetry according to the 3d orbital that is occupied (dσ, dπ, dδ) and to the spin coupling. The $^3\Sigma^-$ state has a formal σ single two-electron chemical bond (singlet-coupled pair), a $4s^2$ pair, and the two spectator 2pπ electrons on N triplet coupled. The Lewis structure is



For each of these remaining five symmetries, the molecular

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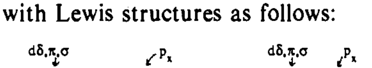
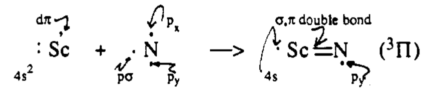
(10) Publications of the experimental groups on neutral metal nitride dimers include: (a) Howard, J. C.; Conway, J. G. *J. Chem. Phys.* **1965**, *43*, 3055. (b) Dunn, T. M.; Rao, K. M. *Nature* (*London*) **1969**, *222*, 266. (c) Dunn, T. M.; Hanson, L. K.; Rubinson, K. A. *Can. J. Phys.* **1970**, *48*, 1657. (d) Bates, J. K.; Ranieri, N. L.; Dunn, T. M. *Can. J. Phys.* **1976**, *54*, 915. (e) DeVore, T. C.; Gallaher, T. N. *J. Chem. Phys.* **1979**, *70*, 3497. (f) Douglas, A. E.; Veillette, P. M. *J. Chem. Phys.* **1980**, *72*, 5378. (g) Dunn, T. M.; Peter, S. L. *J. Chem. Phys.* **1989**, *90*, 5333. (h) Simard, B.; Masoni, C.; Hackett, P. A. *J. Mol. Spectrosc.*, in press. (i) Bates, J. K.; Gruen, D. M. *J. Mol. Spectrosc.* **1979**, *78*, 284. (j) Knight, L. B.; Steadman, J. *J. Chem. Phys.* **1982**, *76*, 3378. (k) Carlson, R. C.; Bates, J. K.; Dunn, T. M. *J. Mol. Spectrosc.* **1985**, *110*, 215. (l) Femenias, J.-L.; Athenour, C.; Rao, K. M.; Dunn, T. M. *J. Mol. Spectrosc.* **1988**, *130*, 269. (m) Bates, J. K.; Gruen, D. M. *J. Chem. Phys.* **1979**, *70*, 4428. (n) Green, D. W.; Reedy, G. T. *J. Mol. Spectrosc.* **1979**, *74*, 423.

(11) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; *Molecular Spectra and Molecular Structure* VI; Van Nostrand: New York, 1979.

configuration along the adiabatic potential curve could evolve from the ground-state atoms, which would have a repulsive interaction due to the $4s^2$ and no formal two-electron bonds to a structure that has an in situ excited-state Sc and has a σ bond and a singly occupied 4s orbital instead of the $4s^2$ pair and singly occupied N $2p\sigma$. Schematically we may represent the $^5\Sigma^-$, $^5\Pi$, $^5\Delta$, and $^3\Delta$ states with Lewis structures as follows:

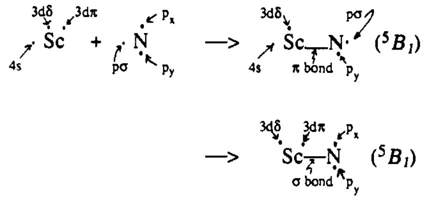


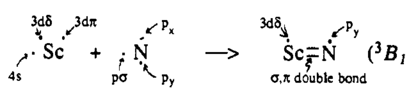
The $^5\Delta$ state of ScN is obtained by coupling a Sc σ and the N $2p\sigma$ to form a σ single bond and coupling the singly occupied Sc 4s and $3d\delta$ and the two N 2 $p\pi$ electrons into a qunitet. The σ singly bonded $^3\Delta$ state differs from the $^5\Delta$ only in nonbonded intraatomic spin couplings and is obtained from the $^5\Delta$ state by all possible couplings of the Sc 4s and $3d\delta$ and the two N $2p\pi$ electrons into a triplet. The $^5\Pi$ and $^5\Sigma^-$ states are analogous to the $^5\Delta$ state, but have a high-spin $d\pi$ and $d\sigma$ electron, respectively, instead of the high-spin δ electron. The σ,π doubly bonded $^3\Pi$ state is obtained from the $^5\Pi$ state by coupling both a Sc σ orbital and N 2 $p\sigma$ and the Sc $3d\pi_x$ and N $2p\pi_x$ into singlet pairs and triplet coupling the Sc 4s and N $2p\pi_y$.



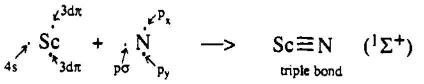
Although we start with the ground-state atoms, as the two atoms approach one another, several electronic configurations of the atoms, including those that contribute to ionic ScN configurations, such as Sc^+N^-, can contribute to the variationally optimized ScN wave function. The molecular configuration along the adiabatic potential curve evolves to that appropriate to the molecular environment with possible $4s^2$–$4p^2$ hybridization of the Sc, $4s$–$3d\sigma$ mixing of the Sc, and contributions from components of excited states of Sc, along with possible $2s$–$2p\sigma$ hybridization of the N and charge transfer.

States of ScN That Correlate with the $3d^24s^1$ a^4F and a^4P Excited States of Sc Atom and Ground-State ^4S N Atom. The $3d^24s^1$ a^4F and a^4P states of Sc can combine with the ^4S state of N to form ScN states of spin 7, 5, 3, and 1 and Σ^+, Π, Δ, and Φ symmetry according to the two 3d orbitals that are occupied ($d\pi d\pi$ or $d\delta d\delta$, $d\sigma d\pi$, $d\sigma d\delta$, $d\pi d\delta$) and to the spin coupling. The septet states with no formal two-electron bonds are assumed to be repulsive and are not considered further. The $^5\Delta$, $^3\Delta$, $^5\Pi$, and $^3\Pi$ states have already been mentioned. The $^1\Delta$ and $^1\Pi$ states are their singlet companions. The $^5B_1$ and $^3B_1$ (mixed Π and Φ in C_{2v} symmetry) states are obtained from Sc with one electron in each of the Sc 4s, $3d\pi_x$, and $3d\delta_-$ orbitals, which is a mixture of the a^4F and $a^4P(4s^13d^2)$ excited states. A $^5B_1$ state of ScN results by either coupling the Sc $3d\pi_x$ and N $2p\pi_x$ to form a π bond or coupling the Sc 4s and N $2p\sigma$ to form a σ single bond and coupling the remaining electrons to form a quintet state. The corresponding formally $\sigma\pi$ doubly bonded $^3B_1$ ScN state results by forming both bonds and $^1B_1$ is its singlet companion. The molecular configuration along the adiabatic potential curve can evolve with possible contributions from components of Sc states with $4s^13d^14p^1$, $3d^24p^1$, and $3d^3$ configurations resulting in $4s$–$3d\sigma$ and $3d$–$4p$ mixing of the Sc, along with possible, $2s$–$2p\sigma$ hybridization of the N and charge transfer.

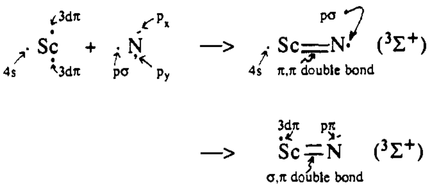




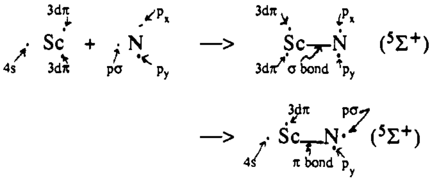
Since Sc and N both have three valence electrons a state of some interest, which corresponds to the maximum number of formal bonds, is the triply bonded $^1\Sigma^+$ state. If N is to dissociate to its ^4S state, the Sc atom must also be in a quartet spin state and by symmetry this should be a configuration with a σ and two π orbitals. A $^1\Sigma^+$ state is obtained from Sc with one electron in each of the Sc 4s, $3d\pi_x$, and $3d\pi_y$ orbitals, which is a mixture of the a^4F and a^4P $(4s^13d^2)$ states. Thus, the molecular configuration along the adiabatic potential curve might evolve with significant $4s$–$3d\sigma$ mixing of the Sc.



The companion $^3\Sigma^+$ state has the same Sc orbital occupation as the $^1\Sigma^+$ state, but with two spins unpaired to form a triplet state. It corresponds to either the formally π,π doubly bonded ScN where the σ bond has been broken or the formally σ,π doubly bonded ScN analogue.



The $^5\Sigma^+$ state can be formed from the $^1\Sigma^+$ state by breaking two bonds. It corresponds to either the formally σ singly bonded ScN where the π bonds in the $^1\Sigma^+$ state are broken and the electrons are coupled into high spins or the formally π singly bonded ScN where the Sc 4s and $3d\pi$ and N $2p\sigma$ and $2p\pi_x$ spectator electrons have high spin.



Alternatively, $^5\Sigma^+$, $^3\Sigma^+$, and $^1\Sigma^+$ states (not shown) with a different Sc orbital occupation result if we move the $3d\pi$ electrons on Sc to the $3d\delta_+$ and $3d\delta_-$ orbitals.

States of ScN That Correlate with the Excited $3d^3$ e^4F and e^4P States of Sc Atom and Ground-State ^4S N Atom. Similarly, the $3d^3$ e^4F and e^4F states of Sc can combine with the ^4S state of N to form ScN states of spin 7, 5, 3, and 1 and Σ^+, Π, Δ, and Φ symmetry according to the 3d orbitals that are occupied ($d\sigma d\pi d\pi$ or $d\sigma d\delta dV$, $d\pi d\delta d\delta$, $d\pi d\pi d\delta$, $d\sigma d\pi d\delta$) and to the spin coupling. The septet states with no formal two-electron bonds are assumed to be repulsive and are not considered further. The states of Σ^+ and Φ (B_1) symmetry have already been mentioned and evolve into an $4s^13d^2$ a^4F state or a mixed a^4F- and a^4P-state Sc at the asymptote, respectively. The states of Π and Δ symmetry are new. The π,π doubly bonded $^3\Delta$ ScN state obtained from the pure e^4F $(3d^3)$ excited-state Sc with one electron in each of the Sc $3d\pi_x$, $3d\pi_y$, and $3d\delta_-$ orbitals is analogous to the $^3\Sigma^+$ state with the spectator electron on Sc in the $3d\delta$ orbital instead of the 4s. The $^1\Delta$ state is its singlet companion.

Breaking one bond results in the π singly bonded $^5\Delta$ ScN, a state analogous to the $^5\Sigma^+$ state but with the spectator electron on Sc in the $3d\delta_-$ orbital instead of the 4s. The π singly bonded $^5\Pi$ ScN state is obtained from Sc with one electron in each of the Sc $3d\pi_x$, $3d\delta_+$, and $3d\delta_-$ orbitals, which is a mixture of the e^4F and e^4F $(3d^3)$ states and is analogous to the $^5B_1$ state with a formal single π bond but with the electron on Sc in the $3d\delta_+$ orbital instead of the 4s. The π singly bonded $^3\Pi$ and $^1\Pi$ ScN

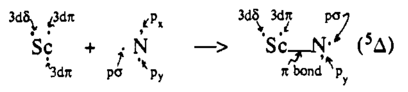
Table I. Scandium Nitride Bond Energies (kcal/mol) Relative to the Ground-State Atoms, Bond Lengths (Å), and Vibrational Frequencies (ω_e, cm^{-1})

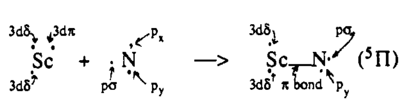
		bond energies			bond lengths			vibrational frequencies		
ScN state	IRR C_{2v}	MCSCF	MCSCF+1+2	MCSCF-(N2S)+1+2	MCSCF	MCSCF+1+2	MCSCF-(N2S)+1+2	MCSCF	MCSCF+1+2	MCSCF-(N2S)+1+2
					σ Single Bonds					
$^3\Sigma^-$	$^3A_2$	6.8	30.4	27.3	2.065	2.051	2.058	553	587	577
$^5\Sigma^-$	$^5A_2$	−11.7	7.0	5.6	2.267	2.247	2.250	404	407	400
$^5\Pi$	$^5B_2$	−5.7	14.5	10.3	2.211	2.198	2.231	485	480	438
$^5\Delta$	$^5A_1$	5.9	25.7	21.1	2.157	2.149	2.173	525	528	489
$^3\Delta$	$^3A_1$	3.9	23.3	18.9	2.168	2.156	2.178	520	531	491
$^1\Delta$	$^1A_1$	−0.3	21.9	17.3	2.174	2.159	2.179	530	546	496
					π Single Bonds					
	$^5B_1$	−4.8	15.0	13.7	2.061	2.051	2.059	584	583	576
$^5\Sigma^+$	$^5A_1$	−13.4	1.5	2.4	2.103	2.092	2.102	549	535	530
					σ,π Double Bonds					
$^3\Pi$	$^3B_2$	23.5	53.2	50.6	1.830	1.839	1.839	809	799	802
$^1\Pi$	$^1B_2$	23.3	52.3	49.8	1.838	1.844	1.845	790	789	789
	$^3B_1$	−2.6	19.8	17.8	2.078	2.048	2.061	574	559	566
					π,π Double Bonds					
$^3\Sigma^+$	$^3A_1$	26.0	56.0	55.3	1.777	1.769	1.769	868	860	861
$^3\Delta$	$^3A_2$	−18.5	13.0	11.7	1.840	1.827	1.830	805	795	790
$^1\Delta$	$^1A_2$	−19.0	11.8	10.5	1.852	1.839	1.843	799	790	785
					σ,π,π Triple Bonds					
$^1\Sigma^+$	$^1A_1$	37.3	64.9	62.7	1.723	1.762	1.768	708	774	726

Table II. Scandium Nitride Dipole Moments (μ, Debye, at R_{eq} with Polarity Sc^+N^-) from the MCSCF Wave Functions and First Anharmonicity Constants ($\omega_e x_e$, cm^{-1}), Rotational Constant (β_e, cm^{-1}), Vibration–Rotation Constant (ϵ_e, cm^{-1}), and Centrifugal Distortion Constant (d_e, cm^{-1}, $\times 10^{-6}$) from the MCSCF(N2S)+1+2 Level Calculation

ScN state	IRR C_{2v}	μ	$\omega_e x_e$	β_e	α_e	d_e
		σ Single Bonds				
$^3\Sigma^-$	$^3A_2$	1.75	5.2	0.373	0.0038	0.623
$^5\Sigma^-$	$^5A_2$	2.36	3.8	0.312	0.0036	0.760
$^5\Pi$	$^5B_2$	3.78	3.8	0.317	0.0029	0.668
$^5\Delta$	$^5A_1$	3.67	3.9	0.334	0.0033	0.623
$^3\Delta$	$^3A_1$	3.59	3.7	0.333	0.0032	0.611
$^1\Delta$	$^1A_1$	3.62	9.6	0.332	0.0039	0.599
		π Single Bonds				
	$^5B_1$	2.34	3.5	0.373	0.0030	0.625
$^5\Sigma^+$	$^5A_1$	2.26	3.1	0.357	0.0027	0.651
		σ,π Double Bonds				
$^3\Pi$	$^3B_2$	3.79	5.6	0.467	0.0033	0.634
$^1\Pi$	$^1B_2$	3.56	5.5	0.464	0.0034	0.644
	$^3B_1$	2.23	3.5	0.372	0.0025	0.641
		π,π Double Bonds				
$^3\Sigma^+$	$^3A_1$	2.46	5.0	0.505	0.0031	0.694
$^3\Delta$	$^3A_2$	9.38	3.4	0.471	0.0024	0.671
$^1\Delta$	$^1A_2$	9.22	3.6	0.465	0.0025	0.652
		Triple Bonds				
$^1\Sigma^+$	$^1A_1$	5.34	0.3	0.505	0.0003	0.979

states of ScN are its triplet and singlet companions. These singly bonded species are assumed unbound and are not studied.





The term symbols and irreducible representations in C_{2V} symmetry as well as the calculated bond energies and spectroscopic parameters for the ScN species studied are collected in Tables I and II. Since real functions are used, in some instances the molecular state of the ScN has a mixed (M_l = 1, 3) angular momentum and only symmetry (B_1) under C_{2V} is designated.

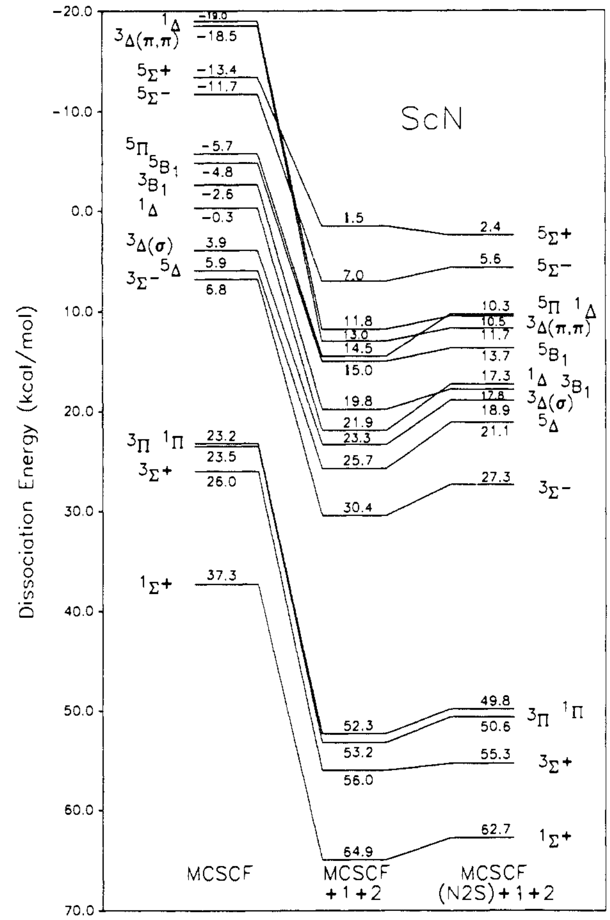


Figure 2. Bond energies of the 15 ScN species calculation at the MCSCF, MCSCF+1+2, and MCSCF(N2S)+1+2 levels showing that the relative order of the states is well described at the MCSCF level and that the N "2s" lone-pair NO should be included in the reference for CI since there is N 2s–2p mixing in the NOs of the MCSCF wave functions.

III. ScN Results

Summary. The bond energies, D_e, referenced to the ground-state atoms, the bond lengths, and the vibrational frequencies at the various levels of theory for the 15 ScN molecules studied are presented in Table I. The bond energies are presented again in Figure 2, where one can see that the relative order of the states is comparably described at the MCSCF and CI levels. The CI

Table III. Characterization of the Scandium Nitride MCSCF Wave Functions at Equilibrium

		valence configuration													gross Sc -> N charge transfer, electron	bonding NO occupation no.	
SCn	IRR	Sc									N						
state	C_{2v}	4s	4pσ	dσ	4p$_x$	dπ_x	4p$_y$	dπ_y	dδ_-	dδ_+	s	pσ	p$_x$	p$_y$		σ	π
σ Single Bonds																	
$^3\Sigma^-$	$^3A_2$	1.53	0.17	0.59	0.08	0.04	0.08	0.04	0.	0.	1.97	1.57	0.96	0.96	0.48	1.95	
$^5\Sigma^-$	$^5A_2$	0.93	0.42	0.97	0.01	0.03	0.01	0.03	0.	0.	1.96	1.72	0.96	0.96	0.60	1.98	
$^5\Pi$	$^5B_2$	0.90	0.24	0.14	0.06	0.97	0.02	0.03	0.	0.	1.97	1.74	0.95	0.97	0.64	1.98	
$^5\Delta$	$^5A_1$	0.87	0.23	0.15	0.02	0.03	0.02	0.03	1.	0.	1.97	1.77	0.95	0.95	0.65	1.98	
$^3\Delta$	$^3A_1$	0.85	0.25	0.16	0.01	0.03	0.01	0.03	1.	0.	1.97	1.76	0.96	0.96	0.66	1.98	
$^1\Delta$	$^1A_1$	0.85	0.26	0.16	0.01	0.03	0.01	0.03	1.	0.	1.98	1.75	0.96	0.96	0.67	1.99	
π Single Bonds																	
	$^5B_1$	0.81	0.21	0.07	0.08	0.18	0.01	0.03	1.	0.	1.94	1.96	1.73	0.96	0.60	(1.00)	1.96
$^5\Sigma^+$	$^5A_1$	0.82	0.20	0.07	0.11	0.20	0.05	0.97	0.	0.	1.95	0.96	1.69	0.98	0.58	(1.00)	1.96
σ,π Double Bonds																	
$^3\Pi$	$^3B_2$	0.82	0.22	0.63	0.09	0.52	0.02	0.07	0.	0.	1.94	1.37	1.37	0.90	0.62	1.92	1.91
$^1\Pi$	$^1B_2$	0.80	0.23	0.64	0.09	0.54	0.01	0.06	0.	0.	1.95	1.37	1.36	0.92	0.62	1.91	1.91
	$^3B_1$	0.79	0.21	0.05	0.10	0.20	0.01	0.02	1.	0.	1.95	0.98	1.68	0.97	0.60	1.33	1.95
π,π Double Bonds																	
$^3\Sigma^+$	$^3A_1$	0.78	0.26	0.17	0.07	0.54	0.07	0.54	0.	0.	1.88	0.90	1.37	1.37	0.56	(1.00)	1.92
$^3\Delta$	$^3A_2$	0.04	0.06	0.13	0.12	0.44	0.12	0.44	1.	0.	1.87	0.90	1.42	1.42	0.63		1.93
$^1\Delta$	$^1A_2$	0.04	0.06	0.12	0.12	0.46	0.12	0.46	1.	0.	1.86	0.92	1.41	1.41	0.62		1.91
Triple Bonds																	
$^1\Sigma^+$	$^1A_1$	0.18	0.26	0.55	0.10	0.61	0.10	0.61	0.	0.	1.86	1.15	1.27	1.27	0.59	1.91	1.92

Table IV. Detailed Atomic Populations of the σ NOs of the Scandium Nitride MCSCF Wave Functions at Equilibrium

		σ bond													
ScN	IRR	Sc			N		Sc singly occupied σ or lone pair					N lone pair		N singly occupied σ	
state	C_{2v}	4s	4pσ	dσ	s	pσ	4s	4pσ	4p$_x$	4p$_y$	dσ	s	pσ	s	pσ
σ Single Bonds															
$^3\Sigma^-$	$^3A_2$	0.01	0.05	0.41	0.09	1.43	1.52	0.12	0.07	0.07	0.18	1.89	0.14		
$^5\Sigma^-$	$^5A_2$	0.17	0.09	0.11	0.18	1.44	0.14	0.03			0.81	1.76	0.25		
							0.63	0.31			0.04				
$^5\Pi$	$^5B_2$	0.05	0.02	0.06	0.45	1.41	0.79	0.17			0.02	1.50	0.32		
$^5\Delta$	$^5A_1$	0.03	0.01	0.06	0.47	1.40	0.80	0.18			0.02	1.50	0.35		
$^3\Delta$	$^3A_1$	0.04	0.02	0.06	0.43	1.43	0.78	0.19			0.02	1.52	0.34		
$^1\Delta$	$^1A_1$	0.03	0.02	0.07	0.45	1.42	0.78	0.20			0.02	1.53	0.34		
π Single Bonds															
	$^5B_1$						0.81	0.19			0.05	1.92	0.03	0.02	0.93
$^5\Sigma^+$	$^5A_1$						0.81	0.18			0.05	1.93	0.03	0.02	0.93
σ,π Double Bonds															
$^3\Pi$	$^3B_2$	0.01	0.03	0.59	0.00	1.36	0.81	0.15			0.04	1.94	0.01		
$^1\Pi$	$^1B_2$	0.01	0.03	0.59	0.01	1.36	0.78	0.17			0.05	1.95	0.01		
	$^3B_1$	0.79	0.19	0.03	0.02	0.96						1.92	0.02		
π,π Double Bonds															
$^3\Sigma^+$	$^3A_1$						0.77	0.21			0.02	1.87	0.01	0.02	0.89
$^3\Delta$	$^3A_2$											1.85	0.01	0.02	0.88
$^1\Delta$	$^1A_2$											1.85	0.02	0.02	0.90
Triple Bonds															
$^1\Sigma^+$	$^1A_1$	0.17	0.20	0.50	0.02	1.15						1.85	0.00		

adds 30 kcal/mol to the dissociation energy of the doubly bonded species (except for σ,π doubly bonded $^3B_1$, which has a very weak σ bond) and the triply bonded species (which has a very weak σ bond) and 20 kcal/mol to that of the singly bonded species and the $^3B_1$ species. There is N 2s–2p mixing in the natural orbitals of the MCSCF wave functions. Thus, including the N "2s" lone-pair natural orbital (NO) in the CI reference space decreases most of the dissociation energies by 2–4 kcal/mol but has little effect on the relative order of the states. We will focus on the MCSCF(N2s)+1+2 level for our discussion. For eight states full potential curves and for three states the equilibrium regions of the MCSCF(N2S)+1+2 potential curves relative to the sum of the ground-state N SCF(N2s)+1+2 and Sc MCSCF(4)+1+2 energies are summarized in Figure 3. The other four states differ from their higher spin partners in nonbonded spin couplings between electrons in distant Sc and N orbitals. Remarkably, all 15 of the variously bonded ScN states studied are bound relative to the ground-state atoms. A comparison of the bond energies and equilibrium bond lengths at the MCSCF(N2S)+1+2 level is presented in Figure 4. The dipole moment from the MCSCF wave functions and other spectroscopic constants from the MCSCF(N2s)+1+2 calculations are presented in Table II. The dipole moments of all 15 ScN states studied are large with polarity Sc$^+$N$^-$. Thus, we expect that an electron could easily add to form a ScN −1 anion. For those states with a spectator electron in the "4s" orbital, this orbital is distended behind the Sc, creating charge separation in the direction opposite to the S to N charge transfer of the bond(s). Thus, the dipole moment is largest for those states without a spectator electron in the "4s" orbital.

Characterization of the equilibrium MCSCF wave functions, including total atomic orbital composition of the valence orbitals and gross Sc to N charge transfer from Mulliken populations, and the natural orbital (NO) occupation numbers of the bonding partner for each bond are presented in Table III. The atomic

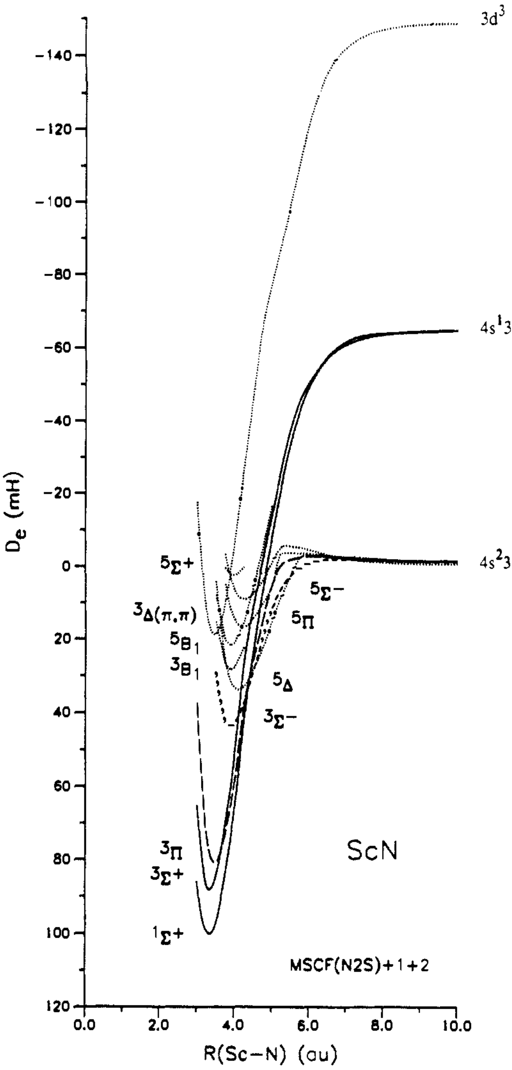


Figure 3. Full potential energy curves for eight of the variously bonded ScN states and the equilibrium regions of the potential curves for three states as a function of internuclear separation for the MCSCF(N2S)+1+2 calculations relative to the ground-state N SCF+1+2 and Sc MCSCF(4)+1+2 energies. The potential curves for the other four species, which differ from their higher spin counterparts only in nonbonded interatomic spin couplings between electrons in distant Sc and N orbitals, are not displayed. The energy units are millihartrees and 1 millihartree equals 0.6257 kcal/mol.

orbital composition of the σ orbitals is broken down in Table IV. While the limitations of the Mulliken population analysis[12] preclude detailed arguments based on them, we are confident of the trends. The important features are the following: for all states the molecular configuration corresponds to a mixture of Sc atomic states; the natural orbitals exhibit N 2s–2p mixing, which we consider to be various degrees of hybridization; bonding in all states has significant ionic Sc^+N^- character due to charge transfer from Sc to N; remarkably, regardless of the number of formal bonds in the various ScN species, the gross Sc to N charge transfer is relatively constant (av 0.62e, spread 0.11e) for all 14 of the scandium nitrides studied that have an excited-state Sc atom in situ and is somewhat larger than that (0.48e) for the one state ($^3\Sigma^-$) with a $4s^23d^1$ ^2D ground-state Sc atom in situ with its $4s^2$ intact. The charge transfer appears to depend only the ionization potential (IP) for the particular in situ Sc configuration.

The Ground and First Excited States of ScN Both Correlate with the Excited-State $4s^13d^2$ a^4F and a^4P Sc Atom and Ground-State ^4S N Atom. We find the ground state of ScN to be the triply bonded $^1\Sigma^+$ state with a dissociation energy relative

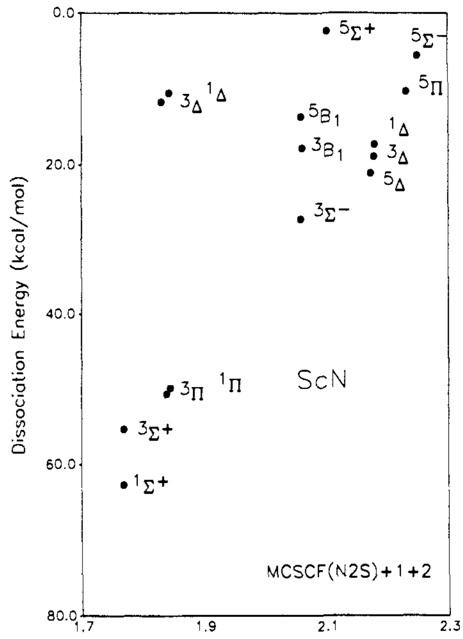


Figure 4. Comparison of the bond energies and equilibrium bond lengths for the 15 variously bonded ScN species at the MCSCF(N2S)+1+2 level.

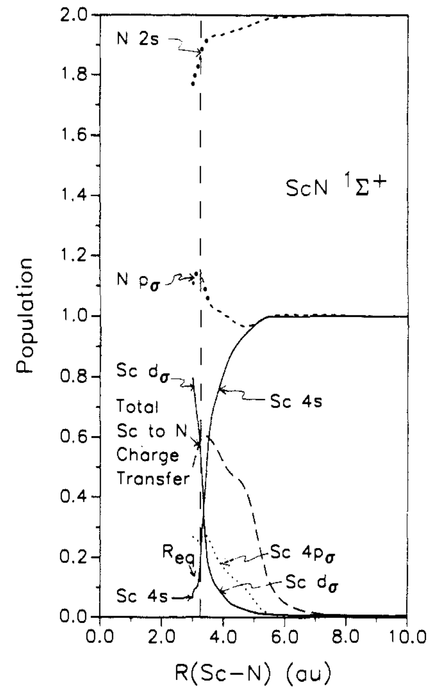


Figure 5. Total valence electron population of selected atomic orbitals of σ symmetry from the valence natural orbitals of the 37 CSF MCSCF wave function and gross Sc to N charge transfer of the triply bonded $^1\Sigma^+$ ScN as a function of internuclear separation. R_{eq} designates the calculated bond length.

to the ground-state atoms of 62.7 kcal/mol. The potential curve in Figure 3 shows that is separates to an excited-state Sc atom and is bound by 104.3 kcal/mol with respect to the asymptotic atoms. Figure 5, which presents the σ atomic orbital populations of the MCSCF valence orbitals as a function of internuclear distance, shows that the singlet coupling of the electrons of the σ bond permitted the 4s to evolve into an mixture of 4s and 3dσ, which is very sensitive to the internuclear distance near equilibrium. It turns out that the σ bond in this molecule is rather weak and one may form a low-lying π,π doubly bonded $^3\Sigma^+$ state by triplet coupling the σ bonding electrons. The alternative coupling (formally σ,π doubly bonded $^3\Sigma^+$ ScN) is higher in energy and

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[12] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343. For a critique, see: Noell, J. O. *Inorg. Chem.* **1982**, *21*, 11.

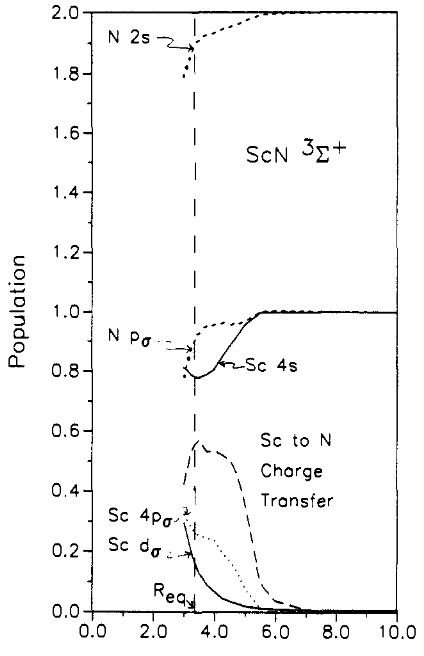


Figure 6. Total valence electron population of selected atomic orbitals of σ symmetry from the valence natural orbitals of the 39 CSF MCSCF wave function and gross Sc to N charge transfer of the π,π doubly bonded $^3\Sigma^+$ ScN as a function of internuclear separation. R_{eq} designates the calculated bond length.

does not contribute at equilibrium but appears to be important at longer bond distances where the σ bond involves the 4s. Interestingly, breaking this σ bond has no effect on the bond length (1.77 Å for both $^1\Sigma^+$ and $^3\Sigma^+$) and reduces the bond energy by only 7.4 kcal/mol (D_e is 55.3 kcal/mol for $^3\Sigma^+$). The molecule in either of these states is held together by the two π bonds, with the very weak σ bond of the $^1\Sigma^+$ state contributing very little. The de facto weakness of the σ bond is due to an energetic compromise between the strength of a triple bond where Sc uses its 3dσ (the 4s is not effective in bonding to N at the bond lengths where the Sc 3dπ will bond with the N 2p$_\pi$) and replacing the 4s with a high-energy Sc 3dσ orbital, i.e., promoting the Sc from the 4s^{1}3d^2 to the 3d^3 configuration. The NO occupation numbers in the region of the minimum presented in Table III show that the σ bond does not have more open-shell character than the π bonds. In contrast with the $^1\Sigma^+$ situation, triplet coupling the two valence σ orbitals results in the σ_{Sc} staying essentially 4s and the σ_N remaining the N 2pσ orbital. This is shown in Figure 6, where we present the evolution of the atomic orbital populations of the MCSCF valence orbitals of σ symmetry for this state as a function of internuclear distance. The π bonds are polarized toward N, and at equilibrium, the two electrons in one π bond are partitioned with 1.4 on N and 0.6 on Sc for the $^3\Sigma^+$ case and 1.3 and 0.7, respectively, for the $^1\Sigma^+$ case. For both states the gross Sc to N charge transfer as a function of internuclear distance is a maximum at the equilibrium bond distance. Figure 7 displays the dipole moments (with polarity Sc$^+$N$^-$) as a function of the bond distance near equilibrium. The $^3\Sigma^+$ state has a fairly constant dipole moment near equilibrium, but the dipole moment for the $^1\Sigma^+$ state varies dramatically near equilibrium concomitant with the change in character of the Sc σ bonding orbital. The total density for both states from the MCSCF wave functions, as well as the density difference near equilibrium between these two states, is presented in Figure 8. R = 3.35 au was chosen for these plots since it is near the MCSCF+1+2 R_{eq} for both states. The dominant feature in the latter plot is the greater density (solid contours) in the region of the Sc 3dσ in the $^1\Sigma^+$ state than in the $^3\Sigma^+$ state. The relative density deficit (dashed contours) in the region around Sc within one-fourth of the Sc–N distance is due to the subtraction of the density buildup inside the outer node in the Sc 4s atomic orbital of the $^3\Sigma^+$ state. There are dashed contours from subtracting the density of the diffuse 4s of the $^3\Sigma^+$ state in regions beyond this node, but they are below the lowest contour used, 0.0125e (each contour differs from its neighbor by a factor of 2). The 3dσ character for the $^1\Sigma^+$ state is much greater at 3.25 au, near the MCSCF R_{eq}. The consequences of the weak σ bond are explored latter in section IV.

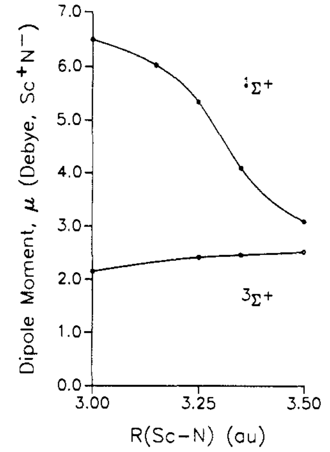


Figure 7. Dipole moment (μ, Debye with polarity Sc$^+$N$^-$) from the natural orbitals of the MCSCF wave function for the triply bonded $^1\Sigma^+$ ScN and the π,π doubly bonded $^3\Sigma^+$ ScN as a function of internuclear separation. R_{eq} designates the calculated bond length.

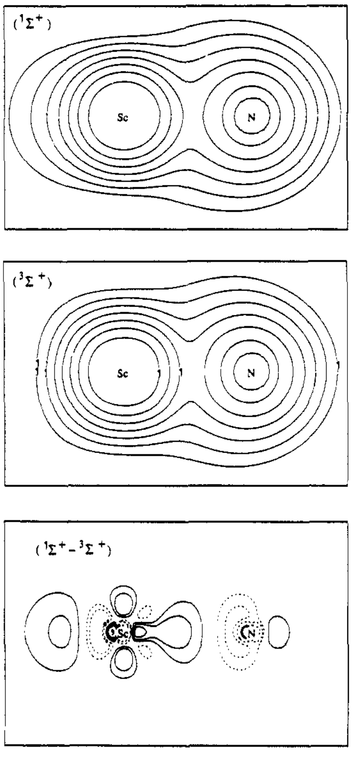


Figure 8. Density contour plots. (a, top) total charge density of the tiply bonded $^1\Sigma^+$ ScN state. (b, middle) total charge density of the π,π doubly bonded $^3\Sigma^+$ ScN state. (c, bottom) charge density difference between the $^1\Sigma^+$-state and the $^3\Sigma^+$-state ScN. R = 3.35 au in all three plots. In all density contour plots in this paper each successive contour differs from its neighbor by a factor of 2 and the lowest contour is 0.0125e.

States of ScN That Dissociate to the Ground-State ^{2}D Sc and ^{4}S N Atoms. Tables III and IV of the atomic orbital populations show that at equilibrium the $^3\Sigma^-$ state has an in situ 4s^{2}3d^1 ^{2}D ground-state Sc and a formal σ single bond with the Sc bond character 3dσ with a slight amount of 4pσ and with the 4s^2 pair essentially intact but polarized with 4pσ. This bond is highly polarized toward N and at equilibrium the two electrons are partitioned with 1.5 on N and 0.5 on Sc. The distance dependence of the atomic orbital populations of the MCSCF valence orbitals (Figure 9) shows that the 4s^2 starts to become mixed with 4pσ

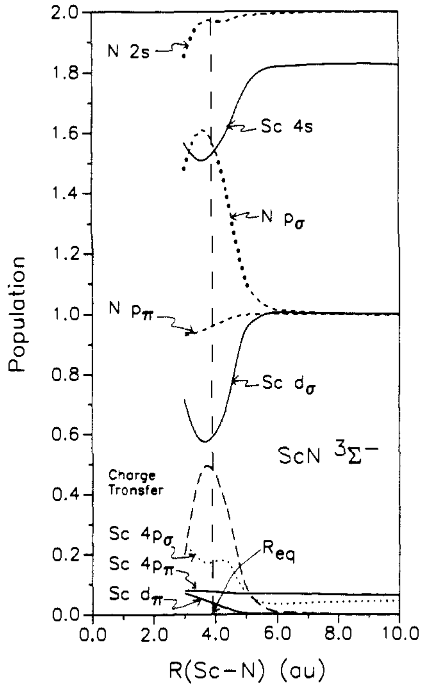


Figure 9. Total valence electron population of selected atomic orbitals of σ and π symmetry from the valence natural orbitals of the 20 CSF MCSCF wave function and gross Sc to N charge transfer of σ singly bonded $^3\Sigma^-$ ScN as a function of internuclear separation. R_{eq} designates the calculated bond length. Note: only one of the two identical π's is pictured.

when the Sc 3dσ to N 2pσ charge transfer in the σ bond begins. The gross Sc to N charge transfer is a maximum near the equilibrium bond distance. Although there are six molecular species that trace their lineage to the ground-state atoms, five of the states have an in situ excited state of Sc rather than the ground state. For the $^5\Sigma^-$, $^3\Pi$, $^5\Pi$, $^3\Delta$, and $^5\Delta$ species, as the two ground-state atoms approach each other, the molecular configuration along the adiabatic potential curve evolves from the ground-state atoms with a $4s^2$ pair on Sc and singly occupied 2pσ on N to a second structure with a σ two-electron bond and a singly occupied Sc 4s orbital corresponding to an in situ excited-state Sc with the $4s^13d^2$ or $4s^14p^13d^1$ configurations. The changes in the atomic orbital populations accompanying this are shown in Figure 10 for the σ singly bonded $^5\Delta$ state. The $4s^2$ pair evolves into a chemical bonding pair while the 2pσ on N evolves into a singly occupied 4s orbital on Sc. At intermediate internuclear separations, the $4s^2$ pair becomes uncoupled and one electron moves to the 3dσ orbital once it is formally coupled to the N 2pσ in a σ bond while the other 4s–4p hybridizes to the rear of the Sc. At the equilibrium bond length the second structure dominates with the Sc component to the σ bond primarily 4pσ for the $^5\Sigma^-$ state and 3dσ for the $^3\Pi$, $^5\Pi$, $^3\Delta$, and $^5\Delta$ states. These states differ in that in the $^5\Sigma^-$, $^5\Pi$, $^3\Delta$, and $^5\Delta$ states the singly occupied spectator orbital is 3dσ, $3d\pi_x$, $3d\delta_-$, and $3d\delta_-$, respectively, whereas the $^3\Pi$ state has a π bond in addition to the σ bond. For the σ singly bonded $^5\Sigma^-$, $^5\Pi$, $^3\Delta$, and $^5\Delta$ states the σ bond is even more polarized toward N than in the $^3\Sigma^-$ state. For the σ,π doubly bonded $^3\Pi$ state the charge transfer toward N is divided equally between both bonds, as shown in Tables III and IV of the equilibrium atomic populations. Thus, the total Sc to N charge transfer is the same (av. 0.63e) in all five species and larger than in the $^3\Sigma^-$ (0.48e) species. For all six states the gross Sc to N charge transfer as a function of internuclear distance is a maximum at the equilibrium bond distance. In summary, of these six states the more stable species is the σ,π double bonded $^3\Pi$ state with a D_e of 50.6 kcal/mol, which is 12.1 kcal/mol above the ground state. Of these five σ singly bonded species, the $^5\Sigma^-$ state is the most stable at 27.3 kcal/mol. The $^5\Delta$ and $^3\Delta$ pair of states, which differ in their nonbonded intraatomic spin couplings, are close behind at 21.1 and 18.9 kcal/mol, respectively. High-spin π–π repulsions make the $^5\Pi$ state at 10.3 kcal/mol less stable than the $^5\Delta$ state and that the $^5\Sigma^-$ state is bound by 5.6 kcal/mol shows the importance of the Sc^+N^-ionic contribution to the bond strength.

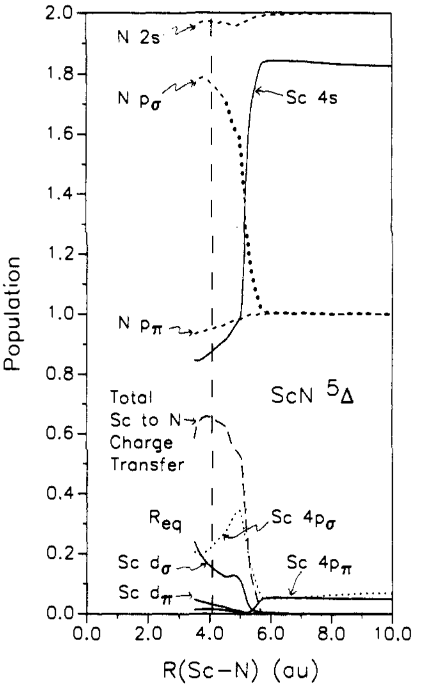


Figure 10. Total valence electron population of selected atomic orbitals of σ symmetry including contribution from $4s^2$–$4p^2$ near-degeneracy correlation from the valence natural orbitals of the 9 CSF MCSCF wave function and gross Sc to N charge transfer of σ,π doubly bonded $^5\Delta$ ScN as a function of internuclear separation. R_{eq} designates the calculated bond length.

Other States of ScN That Correlate with $4s^13d^2$ a^4F and a^4P Excited States of Sc Atom and Ground-State 4S N Atom. Since the σ,π doubly bonded $^1\Pi$ and the σ singly bonded $^1\Delta$ states differ from the corresponding triplets described above only by intraatomic spin couplings between nonbonded electrons, they are only slightly less stable. The equilibrium structure of the $^5\Sigma^+$ state with the same formal Sc orbital occupation as the $^1\Sigma^+$ and $^3\Sigma^+$ states corresponds predominantely to the formally π singly bonded ScN where the Sc 4s and 3dπ and N 2pσ and $2p\pi_x$ spectator electrons have high spin. The π bond is highly polarized toward N, with the gross Sc to N charge transfer being 0.58e at equilibrium. However, the two sets of nonbonded high-spin repulsions offset the ionic stabilization and make the $^5\Sigma^+$ state the least stable species studied, with a bond energy of only 2.4 kcal/mol.

The σ,π doubly bonded $^3B_1$ ScN state is higher in energy than the σ,π doubly bonded $^3\Pi$ ScN state. Formally, it differs in the Sc spectator electron being in the $3d\delta_-$ orbital instead of the 4s. However, like the $^1\Sigma^+$ state, the σ bond in the $^3B_1$ ScN state is extremely weak and one may form a low-lying π singly bonded $^5B_1$-state ScN by triplet coupling the σ bonding electrons. The alternative coupling (formally σ doubly bonded $^5B_1$ ScN) is higher in energy and hardly contributes. Again, breaking this σ bond has no effect on the bond length (2.06 Å for both $^3B_1$ and $^5B_1$) and reduces the bond energy by only 4.1 kcal/mol (D_e is 17.8 and 13.7 kcal/mol for $^3B_1$ and $^5B_1$, respectively). The molecule in either of these states is held together by the single π bond with the very weak σ bond of the $^3B_1$ state contributing slightly. In contrast with the $^1\Sigma^+$ situation, in $^3B_1$ the σ_{Sc} remains essentially 4s despite the singlet coupling of the two valence σ orbitals, since the energetic compromise between a double bond and the stability of the Sc states of the $4s^13d^2$ configuration relative to the states of the $3d^3$ configuration is more severe. Likewise an NO occupation number of 1.33e for the bonding partner of the σ bond reflects the weakness of the bond. The charge transfer occurs only in the π bond, which is polarized toward N. At equilibrium the two electrons in the π bond are partitioned with 1.7 on N and

0.3 on Sc for both the $^3B_1$ and $^5B_1$ states. The density difference near equilibrium between these two states is almost featureless compared to that of the $^1\Sigma^+$–$^3\Sigma^+$ pair since both $^3B_1$ and $^5B_1$ states have basically the same atomic orbitals occupied and the same charge transfer. The gross Sc to N charge transfer is also a maximum at the equilibrium bond distance for these states.

States of ScN That Correlate with Excited-State $3d^3$ e^4F or e^4P Sc and Ground-State ^4S N Atoms. The states with formal π,π double bonds but with the spectator electron on Sc in the $3d\delta_-$ orbital instead of the 4s are the $^3\Delta$ and $^1\Delta$ ScN states, which have in situ pure e^4F $3d^3$ Sc but, remarkably, are bound relative to the ground-state atoms. The bond lengths are shorter than that of the singly bonded species. However, these are longer than that of the π,π doubly bonded $^3\Sigma^+$ species. There is more $4p\pi$ character in the bonds, suggesting stabilization by mixing in states of the $3d^24p^1$ configuration of Sc. The gross Sc to N charge transfer is also a maximum at the equilibrium bond distance for these states.

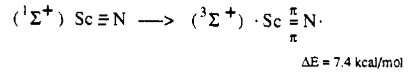
Energetics. Figure 4 and Table I show that, for the σ and π singly bonded species, the calculated D_e vary widely but the four lowest energy multibonded species have a D_e roughly twice that of the most stable singly bonded species, the σ singly bonded $^3\Sigma^-$, which has an in situ ground-state Sc and a dissociation energy of 27.3 kcal/mol. The ScN species of lowest energy is predicted to the triply bonded species $^1\Sigma^+$ with a dissociation energy with respect to the ground-state atoms of 62.7 kcal/mol. Breaking the σ bond of this $^1\Sigma^+$ state to produce the π,π doubly bonded $^3\Sigma^+$ species costs only 7.4 kcal/mol. Likewise, breaking the σ bond of the σ,π doubly bonded $^3B_1$ state to produce the π singly bonded $^5B_1$ species costs only 4.1 kcal/mol. Breaking a π bond is so much more costly that the alternative bonding, σ,π double bond for the $^3\Sigma^P$ state and σ single bond for the $^5B_1$ state, hardly contributes. This suggests that if bonding forces the Sc 4s electron to either be a bonding participant or be promoted to the $3d\sigma$ orbital resulting in an in situ $3d^3$ Sc atom, then the contribution to the bond strength is much less for the σ bond than for a π bond. The σ,π doubly bonded $^3\Pi$ and π,π doubly bonded $^3\Sigma^+$ species in which a spectator electron occupies the 4s have very similar dissociation energies of 50.6 and 55.3 kcal/mol, respectively, only 12.1 and 7.4 kcal/mol above the ground state. The π singly bonded $^5B_1$ species with high-spin repulsions in the σ system has a dissociation energy of 13.7 kcal/mol, while the σ singly bonded $^5\Pi$ species with high-spin repulsions in one π system has a dissociation energy of 10.3 kcal/mol. Again, these two species in which a spectator electron occupies the 4s have very similar dissociation energies. This demonstrates that if the 4s is occupied by a spectator electron the contribution of σ and π bonds to the bond strength is similar, i.e., the σ bonds are weak. This also explains why, given the opportunity for either σ single bonding or π single bonding, the σ single bond is overwhelmingly dominant for the $^5\Pi$ state but the π single bond is overwhelmingly dominant for the $^5B_1$ state. Thus, unlike bonding in main-group elements, in metal–ligand bonding the π bonds can be as strong as or stronger than σ bonds.

Other factors also determine the relative energies of the species. The π,π doubly bonded $^3\Delta$ species with the spectator electron in a $3d\delta_-$ orbital instead of the 4s orbital is less stable (D_e is 11.7 kcal/mol) than the π,π_- doubly bonded $^3\Sigma^+$ species by 33.4 kcal/mol. This is half the calculated SCF+1+2 $4s^13d^2$ a^4F to $3d^3$ e^4F promotion energy of the Sc atom (66.2 kcal/mol), perhaps because $4p\pi$ character in the bonds from in situ mixing with the more stable $4p^23d^1$ Sc states lowers the energy (and lengthens the bond) of the $^3\Delta$ state and penetration of the diffuse Sc 4s by the N destabilizes the $^3\Sigma^+$ state. The σ singly bonded $^5\Pi$ species with a dissociation energy of 10.3 kcal/mol is less stable than the $^5\Delta$ species by 10.8 kcal/mol, due to high-spin repulsions between the $3d\pi_x$ on Sc and the adjacent $2p_x$ on N. Likewise, in addition to the one set of high-spin repulsions in the σ system that they have in common, the high-spin repulsions between the $3d\pi_y$ on Sc and the adjacent $2p_y$ on N make the π singly bonded $^5\Sigma^+$ species (D_e is 2.4 kcal/mol) less stable than the π singly bonded $^5B_1$ species (D_e is 13.7 kcal/mol) by 11.3 kcal/mol. For the σ singly bonded $^5\Delta$, $^3\Delta$, and $^1\Delta$ states, the σ,π doubly bonded $^3\Pi$ and $^1\Pi$ states, and the π,π doubly bonded $^3\Delta$ and $^1\Delta$ states, where the partners differ only in the interatomic spin couplings between nonbonded distance electrons, the higher spin state is slightly more stable by 1–2 kcal/mol.

Equilibrium Nuclear Structural Predictions. Overall the multibonded species have shorter bond lengths than the singly bonded ScN species. Due to the weakness of the σ bonds, the Sc–N π,π double bond of $^3\Sigma^+$ and the triple bond of the ground-state $^1\Sigma^+$ have the same lengths (1.769 Å) and the Sc–N π single bond of $^3B_1$ and the σ,π double bond of $^5B_1$ have the same lengths (2.06 Å). The Sc–N π,π double bond of $^3\Sigma^+$ at 1.769 Å is 0.07 Å shorter than the σ,π double bond of $^3\Pi$ at 1.839 Å. The one state with an in situ ground-state Sc ($^3\Sigma^-$) has a bond length of 2.058 Å, the shortest bond of the σ singly bonded species. However, the π singly bonded $^5B_1$ species (and the σ,π double bond of $^5B_1$) has a similar bond length of 2.059 Å. The other π singly bonded species ($^5\Sigma^+$) has a slightly longer bond length of 2.102 Å due to adjacent high-spin repulsions. The bond length of the five other σ singly bonded species, which have an in situ excited-state Sc, are nearly constant with an average of 2.20 Å and a spread of only 0.07 Å. This suggests that there is a characteristic Sc–N σ single bond length for states with an in situ excited-state Sc. These bond lengths are 0.14 Å longer than that of the $^3\Sigma^-$ state because the 3d orbitals are more expanded in the $4s^13d^2$ a^4F and a^4P excited states of Sc than in the $4s^23d^1$ ^2D ground state of Sc. For the ScN species with an in situ excited-state Sc, the σ single bond average of 2.20 Å is longer than the π single bond average of 2.08 Å. The vibrational frequencies, however, vary for a given bond type.

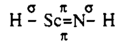
IV. Relevance of These Results to Chemistry

The weakness of the σ bond in the triply bonded $^1\Sigma^1$ ground state of ScN results in the $^3\Sigma^+$ state being only 7.4 kcal/mol higher in energy. The $^3\Sigma^+$ state is a diradical in which the Sc and N each host a high-spin electron.



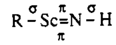
$$({}^1\Sigma^+)\ \mathrm{Sc}\equiv\mathrm{N} \longrightarrow ({}^3\Sigma^+)\ \cdot\mathrm{Sc}\underset{\pi}{\overset{\pi}{=}}\mathrm{N}\cdot \qquad \Delta E = 7.4\ \mathrm{kcal/mol}$$

This suggests that the bond in H_2 might be broken by reaction with $^1\Sigma^+$ ScN to form the linear molecule



$$\mathrm{H}\overset{\sigma}{-}\mathrm{Sc}\underset{\pi}{\overset{\pi}{=}}\mathrm{N}\overset{\sigma}{-}\mathrm{H}$$

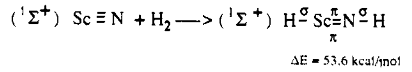
with two Sc–N π bonds. Indeed, the reactions of any alkane R–H should be similar and we anticipate



$$\mathrm{R}\overset{\sigma}{-}\mathrm{Sc}\underset{\pi}{\overset{\pi}{=}}\mathrm{N}\overset{\sigma}{-}\mathrm{H}$$

as the likely product. We note that the bare early-transition-metal atoms will not exothermically break the H–H bond in H_2 or a C–H bond in hydrocarbons.[13]

In order to test our hypothesis we performed ab initio calculations on the linear HScNH species at the MCSCF level. Details of the HScNH calculation are in the Appendix. Indeed, we find that ScN will split H_2 exothermically (by 53.6 kcal/mol at this level) to form a linear HScNH molecule with two Sc–N π bonds. The unexpectedly strong bonding in HScNH, which is due to some dative bonding from the N lone pair to Sc in the σ system, is discussed in detail in another paper.



$$({}^1\Sigma^+)\ \mathrm{Sc}\equiv\mathrm{N} + \mathrm{H_2} \longrightarrow ({}^1\Sigma^+)\ \mathrm{H}\overset{\sigma}{-}\mathrm{Sc}\underset{\pi}{\overset{\pi}{=}}\mathrm{N}\overset{\sigma}{-}\mathrm{H} \qquad \Delta E = 53.6\ \mathrm{kcal/mol}$$

The optimized bond lengths are R(Sc–N) = 2.018 Å, R(Sc–H) = 1.809 Å, and R(N–H) = 1.027 Å.

V. Computational Method

a. The Atoms. Since the molecular wave functions can involve a significant mixing of the low-lying Sc asymptotes, one measure of the quality of the calculation is how well the atomic splittings are reproduced. Table V collects selected the experimental (av-

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[13] Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627.

Table V. Selected Scandium Atom Promotion Energies (kcal/mol) from $3d^14s^2$ ^2D Ground State

Sc excited state					
state	confign	expt[a]	SCF[b]	SCF[c]	SCF+1+2[d]
	Pure Angular Momentum States[e]				
a^4F	s^1d^2	32.8	26.0	43.3	41.2
z^4F^0	$d^1s^1p^1$	45.0	21.3	38.7	39.9
e^4F	d^3	96.4	110.2	124.7	107.8
	Example Mixed Angular Momentum States				
$(^4/_5)^{1/2}\|a^4F\rangle - (^1/_5)^{1/2}\|a^4P\rangle$	$4s^1d\pi_x{}^1d\pi_y{}^1$	36.4[f]	30.6	48.0	41.6
$(^2/_3)^{1/2}\|z^4F^0\rangle - (^1/_3)^{1/2}\|z^4D^0\rangle$	$4s^1d\pi_x{}^14p_y{}^1$	45.3[f]	21.3	38.7	39.9

[a] Reference 9, averaged over values for J states for each term. [b] Relative to SCF ^2D Sc. [c] Relative to MCSCF(4) ^2D Sc (^2D $4s^23d^1$ MCSCF(4) − SCF = 17.4 kcal/mol). [d] Relative to MCSCF(4)+1+2 ^2D Sc. [e] Calculated under C_{2v} symmetry by using energies from Table VIII for the calculation using the real orbital occupancies, which yield the correct spatial symmetry as determined in ref 17. [f] Calculated as indicated weighted average from experimental values of pure states.

Table VI. Number of Configuration-State Functions (CSFs)

ScN state	IRR C_{2v}	MCSCF	MCSCF+1+2	MCSCF(N2S)+1+2
			σ Single Bonds	
$^3\Sigma^-$	$^3A_2$	20	54 863	144 997
$^5\Sigma^-$	$^5A_2$	9[a]	14 370[a]	47 859[a]
$^5\Pi$	$^5B_2$	9	25 459	81 378
$^5\Delta$	$^5A_1$	9	24 983	80 174
$^3\Delta$	$^3A_1$	21	51 549	138 782
$^1\Delta$	$^1A_1$	9	18 947	49 656
			π Single Bonds	
	$^5B_1$	9	17 906	65 131
$^5\Sigma^+$	$^5A_1$	9[ab]	9917[a]	38 162[a]
			σ,π Double Bonds	
$^3\Pi$	$^3B_2$	35	65 380	194 527
$^1\Pi$	$^1B_2$	17	25 182	72 384
	$^3B_1$	25	39 176	121 377
			π,π Double Bonds	
$^3\Sigma^+$	$^3A_1$[c]	25	40 891	128 020
		39	48 723	166 552
$^3\Delta$	$^3A_2$[d]	25	38 915	121 102
$^1\Delta$	$^1A_2$	17	23 735	68 618
			Triple Bonds	
$^1\Sigma^+$	$^1A_1$	37	31 423	100 015

[a] Indicates that the calculation was done without the δ orbitals in order to avoid contamination. [b] Alls pin couplings to allow σ single or π single bond. [c] π,π Double bond. [d] All spin couplings to allow σ,π double or π,π double bond.

eraged over values for J states for each term)[9] and the all-electron ab initio SCF or MCSCF(4) and the SCF+1+2 or MCSCF-(4)+1+2 level calculated energy separations for the (Ar core)-$4s^23d^1$ ground state and the high-spin excited states of $4s^13d^2$, $4s^14p^13d^1$, $4p^13d^2$, and $3d^3$ configurations for Sc. Comparison of the first two columns demonstrates that the SCF level results in a poor separation of the $(3d^14s^2)^2D$ ground state from the excited states of Sc. This is due to the $4s^2$–$4p^2$ near-degeneracy effect. This ^2D Sc state is more properly described by a four-configuration MCSCF wave function where the 4s orbital is correlated with the three 4p orbitals, each doubly occupied in turn. The form of the GVB representation of this four-configuration Sc wave function is as follows:

$$\text{Sc:}\quad {}^2D \sim [4s^2 + \lambda 4p\sigma^2 + \mu 4p\pi_y{}^2 + \mu 4p\pi_x{}^2]$$

Inclusion of this near-degeneracy correlation makes the Sc ^2D 17.4 kcal/mol more stable and results in a more sensible reproduction of the experimental splittings as shown in the third and fourth column of the splitting calculated at the MCSCF(4) and SCF level and at the MCSCF(4)+1+2 and SCF+1+2 level, respectively.

Note also that although experimentally the lowest state, a^4F, of the Sc $4s^13d^2$ configuration is lower in energy than that z^4F, of the $3d^14s^14p^1$ configuration, the SCF calculation inverts this order resulting in that for the $3d^14s^14p^1$ configuration being more stable. Even including the CI as in the fourth column does not correct for this. The difficulty in ordering these two states is well known and has been pointed out by Walch and Bauschlicher[14] to be due to the incompleteness of the basis set and the need for the inclusion of *f* functions in order to allow $3p^2$ to f^2 excitations.

b. The Molecules. MCSCF Wave Function for Structural Correlation, Correlation for $4s^2$–$4p^2$ Near Degeneracy, and Spin-Coupling and Subsequent Dynamical Correlation. The structure of the bond dissociation energy calculations are illustrated below. As examples, we describe the construction of the MCSCF wave function and the CI and present the corresponding potential curves for the $^1\Sigma^+$, $^3\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$ states. The MCSCF wave function for each of the remaining states studied is described in the Appendix, along with general computational details, including the basis sets, and molecular codes.

The Ground State and the First Excited State of ScN Both Correlate with the $3d^24s^1$ a^4F and a^4P Excited States of the Sc Atom and Ground-State ^4S N Atom. $^1\Sigma^+$ σ,π,π Triply Bonded ScN. The ScN molecular state that will admit three formal two-electron bonds between unpaired electrons on N in the $(2s^22p^3)_4S$ state and unpaired electrons on Sc with either the $4s^1d\pi_x{}^1d\pi_y{}^1$ occupation or the $d\sigma^1d\pi_x{}^1d\pi_y{}^1$ occupation has $^1\Sigma^+$ symmetry and is calculated as $^1A_1$ under C_{2V} symmetry. The Sc atom orbital occupations, $4s^1d\pi_x{}^1d\pi_y{}^1$ and $d\sigma^1d\pi_x{}^1d\pi_y{}^1$, do not have pure orbital angular momentum under C_{2V} symmetry, but rather are a mixture of the a^4F and a^4P $3d^24s^1$ and the e^4F and e^4P $3d^3$ states of Sc, respectively. The dominant bond–antibond structural correlation of the bonds is provided in a generalized valence bond (GVB) fashion.[7] The asymptotic form of the GVB ansatz for this state is as follows:

$$^1\Sigma^+\ (^1A_1) \sim [\sigma(\mathrm{Sc})\sigma(\mathrm{N}) + \sigma(\mathrm{N})\sigma(\mathrm{Sc})] \times [\pi_y(\mathrm{Sc})\pi_y(\mathrm{N}) + \pi_y(\mathrm{N})\pi_y(\mathrm{Sc})][\pi_x(\mathrm{Sc})\pi_x(\mathrm{N}) + \pi_x(\mathrm{N})\pi_x(\mathrm{Sc})]$$

where the three spin pairs are (1) σ(Sc) and σ(N), (2) π_y(Sc) and π_y(N), and (3) π_x(Sc) and π_x(N). At large separation σ(N) is the $2p\sigma$ orbital and σ(Sc) is the 4s, π_y(Sc) is the $3d\pi_y$ or $4p\pi_y$ orbital and π_y(N) is the $2p_y$ orbital, and π_x(Sc) is the $3d\pi_x$ or $4p\pi_x$ orbital and π_x(N) is the $2p_x$ orbital. These six orbitals constitute the valence space. In this and in subsequent discussions we will suppress the expression of the 18 electrons in the Ar core on Sc and the 4 electrons in the 1s and 2s orbitals on N. These are, of course, included in the all-electron calculation and are variationally optimized. This perfect pairing GVB wave function does not separate to the pure spin states of the atoms. A multiconfiguration self-consistent-field (MCSCF) function of this form provides the structural correlation of the bonds in the GVB fashion and includes all possible spin couplings among the six valence electrons consistent with the desired spin state. It consists of 37 CSFs and is constructed and solved variationally as a function of the Sc–N separation. The MCSCF function dissociates properly to the sum of the single self-consistent-field (SCF) configuration functions for the atoms in their correct spin state (the molecular asymptote); however, with an orbital occupation reflecting the poor seperation of Sc states, i.e., since the calculated Sc atom $4s^13d^2$ and $4s^14p^13d^1$ SCF energies are not in the experimental order, the SCF products are $[\mathrm{Sc}((^2/_3)^{1/2}|z^4F^0\rangle - (^1/_3)^{1/2}|z^4D^0\rangle) + \mathrm{N}(^4S)]$ with the $4s^14p\pi_x{}^1d\pi_y{}^1$ Sc orbital occupation, a well-defined asymptote.

Dynamical correlation for the six electrons in the MCSCF active space was included using multireference (MR) all singles and doubles (SD) configuration–interaction (CI) (MRSDCI). First, we denote as MCSCF+1+2 the MRSDCI calculation with SD excitations using the entire MCSCF wave functions as reference and from all valence orbitals (no excitations were permitted from the N 2s orbital) in all MCSCF configurations. No excitations were permitted from the Ar core of Sc or the 1s core of N. This

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(14) Walch, S. P.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1983**, *79*, 3590.

Table VII. Total Energies (Hartree) of the Scandium Nitride Species at the Equilibrium Bond Length, R_{eq}, (and Selected Total Energies at the Molecular Asymptote, R = 20.0 au)

ScN state	IRR C_{2v}	MCSCF	MCSCF+1+2	MCSCF-(N2S)+1+2
		σ Single Bonds		
$^3\Sigma^-$	$^3A_2$	−814.16529	−814.23745	−814.31396
		(−814.15451)	(−814.18841)	(−814.26870)
$^5\Sigma^-$	$^5A_2$	−814.13583[a]	−814.19082[a]	−814.25246[a]
		(−814.15451)[a]	(−814.17937)[a]	(−814.24241)[a]
$^5\Pi$	$^5B_2$	−814.14518	−814.21213	−814.28695
		(−814.15423)	(−814.18819)	(−814.26841)
$^5\Delta$	$^5A_1$	−814.16385	−814.22995	−814.30410
		(−814.15423)	(−814.18819)	(−814.26831)
$^3\Delta$	$^3A_1$	−814.16067	−814.22619	−814.30064
$^1\Delta$	$^1A_1$	−814.15409	−814.22396	−814.29804
		π Single Bonds		
	$^5B_1$	−814.14685	−814.21298	−814.29224
$^5\Sigma^+$	$^5A_1$	−814.13309[a]	−814.18210[a]	−814.24723[a]
		σ,π Double Bonds		
$^3\Pi$	$^3B_2$	−814.19190	−814.27382	−814.35113
		(−814.15423)	(−814.18819)	(−814.26846)
$^1\Pi$	$^1B_2$	−814.19158	−814.27244	−814.34984
	$^3B_1$	−814.15040	−814.22064	−814.29888
		(−814.08880)		
		π,π Double Bonds		
$^3\Sigma^+$	$^3A_1$b	−814.19570	−814.27833	−814.35851
		(−814.09281)		(−814.20532)
	c	−814.19573	−814.27834	−814.38561
		(−814.09281)		(−814.20532)
$^3\Delta$	$^3A_2$	−814.12495	−814.20976	−814.28917
		(−814.00007)		(−814.12140)
$^1\Delta$	$^1A_2$	−814.12417	−814.20781	−814.28719
		Trible Bonds		
$^1\Sigma^+$	$^1A_1$	−814.21388	−814.29257	−814.37046
		(−814.09281)	(−814.12493)	(−814.20532)

[a] The calculation was done without the δ orbitals in order to avoid contamination. [b] π,π Double Bond. [c] All spin couplings to allow σ,π double or π,π double bond.

wave function dissociates properly to the single SCF reference configuration (SR) all singles and doubles CI (SRSDCI) calculation, denoted SCF+1+2, for each atom with the singly occupied 4s and 3d orbitals on Sc correlated and the 2p orbitals on N correlated. Second, we denote as MCSCF(N2S)+1+2 a MRSDCI calculation where the doubly occupied N 2s core orbital is also included in the active space for each configuration in the MCSCF. This dissociates to the SCF+1+2 calculation for Sc and, for N, the SRSDCI calculation in which the N 2s is also active, denoted as SCF(N2S)+1+2.

Shown in Figure 11 are the MCSCF potential curve relative to the sum of the ground-state N SCF and Sc MCSCF(4) energies and the MCSCF+1+2 and MCSCF(N2S)+1+2 potential curves relative to the sum of the corresponding ground-state atomic energies. Note that at each theoretical level, the molecular asymptotic energies in Table VII are equal to the sum of the energies of the atoms in Table VIII, i.e., these calculations are size consistent. The MCSCF+1+2 potential curves start to drop in energy at larger distances than the MCSCF curves do, but have the minimum at nearly the same distance. this suggests that the relative contributions of the Sc, Sc^+, N, N^-, and other states to the Sc–N bonds are well described by the MCSCF wave functions at equilibrium but not as well at longer bond distances. Generally, since the MCSCF potential curves follow the CI curves resulting in good equilibrium bond lengths at that level, we are confident that the essential physics is in the MCSCF formulation. But, due to the misordering of the SCF and SCF+1+2 Sc asymptotes with sd^2 and spd configurations, both curves are incorrect at long bond distances. Because of this nonphysical asymptotic order, we have not followed the evolution of the π atomic orbital populations for this state as in the previous studies, but only the σ populations, shown in Figure 5. We are confident that the electron distribution as revealed by the atomic orbital populations and the charge density distribution in the region of the minimum are reliable and the former is presented in Tables III and IV and the latter is presented in Figure 8a.

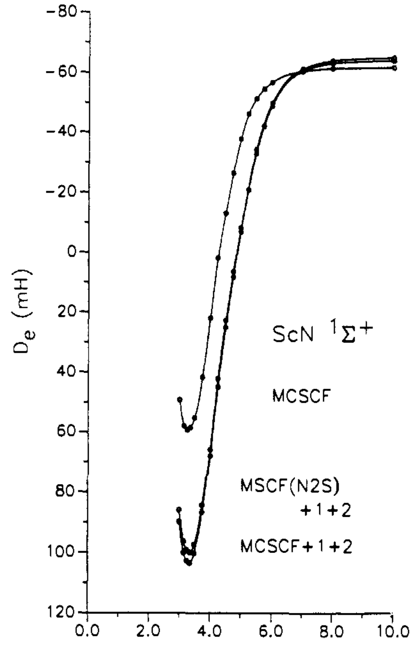

Figure 11. Potential energy curves for the triply bonded $^1\Sigma^+$ state of ScN as a function of internuclear separation for the MCSCF, MCSCF+1+2, and MCSCF(N2S)+1+2 calculations relative to the ground-state atoms. D_e, millihartrees.

$^3\Sigma^+$ π,π Doubly Bonded ScN. The high-spin ScN molecule with either two π spin pairs or one σ and one π spin pair formed by breaking one bond of the $^1\Sigma^+$ state has $^3\Sigma^+$ symmetry ($^3A_1$ under C_{2v} symmetry). The asymptotic form of the GVB representation

Table VIII. Selected N and Sc Atom Total Energies (Hartree)

N state	IRR C_{2v}	valence confign	SCF	SCF+1+2	SCF(N2S)+1+2
a^4S	$^4A_1$	$s^2p\sigma^1p_x^1p_y^1$	−54.40074	−54.42838	−54.50980
		No δ Atomic Orbital Functions Used			
a^4S	$^4A_1$	$s^2p\sigma^1p_x^1p_y^1$	−54.40074	−54.42065	−54.48442

Sc state	IRR C_{2v}	valence confign	SCF	MCSCF(4)[a]	SCF+1+2 SCF(N2S)+1+2
a^2D	$^2A_1{}^b$	$s^2d\sigma^1$	−759.72608	−759.75377[a]	−759.75984[a]
a^4F	$^4A_1{}^b$	$s^1d\sigma^1d\delta_+^1$	−759.68471		−759.69493
z^4F	$^4A_1{}^b$	$s^1p\sigma^1d\delta_+^1$	−759.69207		−759.69711
$(^4/_5)^{1/2}\|a^4F) - (^1/_5)^{1/2}\|a^4P)$	$^4A_2$	$s^1d\pi_x^1d\pi_y^1$	−759.67725		−759.69439
$(^2/_3)^{1/2}\|z^4F^0) - (^1/_3)^{1/2}\|z^4D^0)$	$^4A_2$	$s^1d\pi_x^14p_y^1$	−759.69207		−759.69711
e^4F	$^4A_1{}^b$	$d\pi_x^1d\pi_y^1d\delta_-^1$	−759.55505		−759.58884
		No δ Atomic Orbital Functions Used			
a^2D	$^2A_1{}^b$	$s^2d\sigma^1$	−759.72608	−759.75377[a]	−759.75905[a]

[a] Correlation for $4s^2$–$4p^2$ near-degeneracy in MCSCF. [b] The real orbital occupancy yields the correct spatial symmetry as determined in ref 17.

of the wave function for the π,π double bonded description would be as follows:

$$^3\Sigma^+\ (\pi,\pi)(^3A_1) \sim [\pi_y(\mathrm{Sc})\pi_y(\mathrm{N}) + \pi_y(\mathrm{N})\pi_y(\mathrm{Sc})] \times [\pi_x(\mathrm{Sc})\pi_x(\mathrm{N}) + \pi_x(\mathrm{N})\pi_x(\mathrm{Sc})]\ 4s\ 2p\sigma$$

where the two spin pairs are (1) π_y(Sc) and π_y(N) and (2) π_x(Sc) and π_x(N); and the extra electrons in the N $2p\sigma$ and the Sc 4s are coupled into a triplet. The MCSCF function of this form provides the structural correlation of the bonds in the GVB fashion and includes all possible spin couplings among the six valence electrons consistent with the desired spin state, i.e., that of the spectator electrons in the singly occupied σ spectator orbitals with the bonding electrons. It consists of 25 CSFs and separates to the SCF products in their correct spin states.

Likewise, the asymptotic form of the GVB representation of the wave function for one of the two σ,π double bonded descriptions would be

$$^3\Sigma^+\ (\sigma,\pi)(^3A_1) \sim [\sigma(\mathrm{Sc})\sigma(\mathrm{N}) + \sigma(\mathrm{N})\sigma(\mathrm{Sc})] \times [\pi_x(\mathrm{Sc})\pi_x(\mathrm{N}) + \pi_x(\mathrm{N})\pi_x(\mathrm{Sc})]\ 3d\pi_y\ 2p_y$$

where the two spin pairs are (1) σ(Sc) and σ(N) and (2) π_x(Sc) and π_x(N); and the extra electrons in the N $2p_y$ and the Sc $3d\pi_y$ are coupled into a triplet. The MCSCF function of this form, in addition, includes all possible spin couplings among the six valence electrons consistent with the desired spin state, i.e., that of the spectator electrons in the singly occupied N $2p_y$ and the Sc $3d\pi_y$ spectator orbitals with the bonding electrons. It consists of 25 CSFs and separates to the SCF products.

A MCSCF wave function that allows either the π,π double bond or the σ,π double bond description is generated by starting with the MCSCF wave function for the $^1\Sigma^+$ state and coupling the spins all possible ways to make an overall triplet. This MCSCF function consists of 39 CSFs and, as expected, separates to the SCF products in their correct spin state.

We find π,π double bond overwhelmingly dominant at equilibrium with NO occupation numbers of 1.0 for the σ system, but the σ,π double bond using the 4s is important at intermediate distances, $R = \sim 5.00$ au. Whether only the π,π bond is included in the wave function or whether both the π,π and σ,π bond descriptions are combined in one calculation, we obtain the same description at equilibrium, including D_e, R_{eq}, ω_e, and the other spectroscopic constants, and Mulliken populations. The MCSCF+1+2 and MCSCF(N2S)+1+2 calculations correlate six and eight valence electrons, respectively, i.e., the electrons involved in the bonds as well as the spectator electrons and the N "2s" for the MCSCF(N2s)+1+2. The potential curves at the MCSCF, MCSCF+1+2, and MCSCF(N2S)+1+2 levels for the calculation where both the π,π and σ,π bond descriptions are combined are shown in Figure 12. The potential curve at the MCSCF level for the π,π description is included as a dashed line. Again, the calculations are size consistent and similar R_{eq} are obtained at the three levels.

States of ScN That Dissociate to the Ground-State ^{2}D Sc and ^{4}S N Atoms. $^3\Sigma^-$ σ Singly Bonded ScN. The ScN high-spin molecular state that will admit one formal σ two-electron bond between an electron on Sc in the ($3d^14s^2$) ^{2}D state and an unpaired electron on N in the ($2s^22p^3$) ^{4}S state has $^3\Sigma^-$ symmetry and is calculated as $^3A_2$ under C_{2v} symmetry. The asymptotic form of the GVB representation of the wave function is

$$^3\Sigma^-\ (^3A_2) \sim \sigma(4s)^2[\sigma(\mathrm{Sc})\sigma(\mathrm{N}) + \sigma(\mathrm{N})\sigma(\mathrm{Sc})]\ 2p_x\ 2p_y$$

where the spin pair is σ(Sc) and σ(N), the doubly occupied σ(4s) orbital is the 4s, and the $2p_\pi$ orbitals are triplet coupled. At large separation σ(N) is the $2p\sigma$ orbital and σ(Sc) is the $3d\sigma$. The asymptotic form of the GVB representation of the ScN wave function, which in addition allows for the Sc $4s^2$–$4p^2$ near-degeneracy by including the correlation of the Sc 4s orbital with the three 4p orbitals, each doubly occupied in turn, is as follows:

$$^3\Sigma^-\ (^3A_2) \sim [\sigma(4s)^2 + \lambda\sigma(4p\sigma)^2 + \mu\pi(4p_y)^2 + \mu\pi(4p_x)^2] \times [\sigma(\mathrm{Sc})\sigma(\mathrm{N}) + \sigma(\mathrm{N})\sigma(\mathrm{Sc})]\ 2p_x\ 2p_y$$

where the other orbitals are the same as above. Thus, eight valence atomic orbitals constitute the valence space. The MCSCF wave function of this form with all eight orbitals included in the active space provides the structural correlation of the bonds in the GVB fashion, correlates for the $4s^2$–$4p^2$ near-degeneracy, and includes all possible spin couplings consistent with the desired spin state. It consists of 20 CSFs and dissociates properly to the sum of the four-configuration MCSCF function for the Sc atom correlated at the $4s^2$–$4p^2$ near-degeneracy level and the single SCF configuration function for the N atom, both in their correct spin state [Sc(^{2}D) and N(^{4}S)].

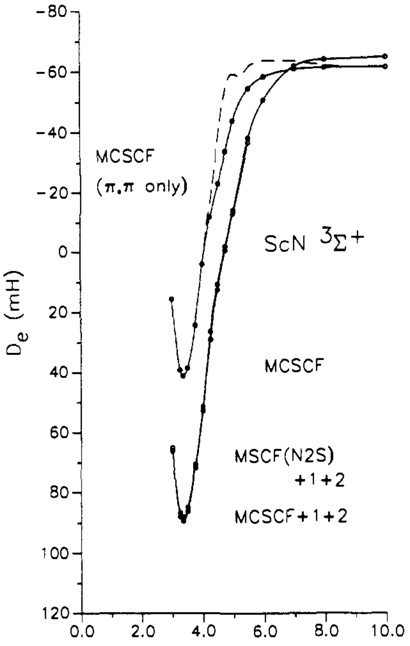

Figure 12. Potential energy curves for the π,π doubly bonded $^3\Sigma^+$ state of ScN as a function of internuclear separation for the MCSCF, MCSCF+1+2, and MCSCF(N2S)+1+2 calculations relative to the ground-state atoms. D_e, millihartrees.

Here, the MCSCF+1+2 calculation correlates the electrons involved in the bond as well as the spectator electrons in the N $2p_\pi$ singly occupied and the Sc doubly occupied 4s or correlating 4p orbitals. It dissociates to the four-configuration reference SDCI calculation, denoted MCSCF(4)+1+2, for the Sc and the SCF+1+2 calculation for the N with the doubly occupied 4s or 4p on Sc correlated and the 2p orbitals on N correlated. The MCSCF(N2S)+1+2 calculation where the doubly occupied N 2s core orbital is also included in the active space for each configuration in the MCSCF dissociates to the MCSCF(4)+1+2 calculation for the Sc and the SCF(N2S)+1+2 calculation for the N.

The potential curves for the three levels of theory are shown in Figure 13 for the $^3\Sigma^-$ state. The bonding region is evident and the bond lengths are similar for all levels of theory. Although the MCSCF curve is repulsive at intermediate bond distances due to $4s^2$ interaction with the incoming N, the MCSCF(N2S)+1+2 and MCSCF+1+2 curves do not show this repulsion.

$^3\Pi$ σ,π Doubly Bonded ScN. The ScN high-spin molecular state of $^3\Pi$ symmetry ($^3B_2$ under C_{2v} symmetry) that will admit one formal π two-electron bond between the unpaired electron on Sc in the ($3d^14s^2$) ^{2}D state and unpaired electrons on N in the ($2s^22p^3$) ^{4}S state evolves into a molecular state with the same symmetry that will also admit one formal σ two-electron bond as well as one formal π two-electron bond between the electron on Sc with the $4s^1d\sigma^1d\pi_x^1$ occupation in the $[-(^2/_5)^{1/2}|a^4F\rangle + (^3/_5)^{1/2}|a^4P\rangle]$ mixed state and an unpaired electron on N in the ^{4}S state. Thus, both states need to be well described by the MCSCF wave function. The asymptotic form of the GVB representation of the former ScN wave function, which is the π singly bonded analogue to that

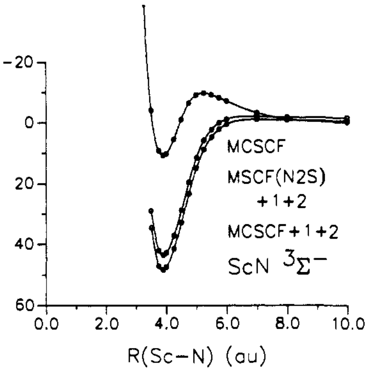

Figure 13. Potential energy curves for the σ singly bonded $^3\Sigma^-$ state of ScN as a function of internuclear separation for the MCSCF, MCSCF+1+2, and MCSCF(N2S)+1+2 calculations relative to the ground-state atoms. D_e, millihartrees.

for the σ singly bonded $^3\Sigma^-$ with the $4s^2$–$4p^2$ near-degeneracy correction included, is as follows:

$$^3\Pi\ (\pi)(^3B_2) \sim [\sigma(4s)^2 + \lambda\sigma(4p\sigma)^2 + \mu\pi(4p_y)^2 + \mu\pi(4p_x)^2][\pi(\mathrm{Sc})\pi(\mathrm{N}) + \pi(\mathrm{N})\pi(\mathrm{Sc})]\ 2p\sigma\ 2p_y$$

where the spin pair is π(Sc) and π(N) and the extra electrons in the N $2p\sigma$ and $2p_y$ orbitals are coupled into a triplet. The asymptotic form of the GVB representation of the latter ScN wave function, which provides for the structural correlation of the σ and the π bonds, is as follows:

$$^3\Pi\ (\sigma,\pi)(^3B_2) \sim [\sigma(\mathrm{Sc})\sigma(\mathrm{N}) + \sigma(\mathrm{N})\sigma(\mathrm{Sc})][\pi(\mathrm{Sc})\pi(\mathrm{N}) + \pi(\mathrm{N})\pi(\mathrm{Sc})]\ 4s\ 2p_y$$

where the spin pairs are (1) σ(Sc) and σ(N) and (2) π(Sc) and π(N); and the extra electrons in the N $2p_y$ and Sc 4s orbitals are coupled into a triplet. The asymptotic form of the combined GVB representation of these two GVB asymptotic wave functions, not duplicating what they have in common, is as follows:

$$^3\Pi\ (\pi)(^3B_2) \sim [\sigma(4s)^2 + \lambda\sigma(4p\sigma)^2 + \mu\pi(4p_y)^2 + \mu\pi(4p_x)^2][\pi(\mathrm{Sc})\pi(\mathrm{N}) + \pi(\mathrm{N})\pi(\mathrm{Sc})]\ 2p\sigma\ 2p_y$$

where the first two terms, $[\sigma_A{}^2 + \lambda\sigma_B{}^2]$, are either the $4s^2$ and the $4p\sigma$ part of the $4s^2$–$4p^2$ near-degeneracy correlation or the $[\sigma(\mathrm{Sc})\sigma(\mathrm{N}) + \sigma(\mathrm{N})\sigma(\mathrm{Sc})]$ structural correlation of the σ bond, the π spin pair is π(Sc) and π(N), σ_C is either the N $2p\sigma$ or the Sc 4s, and the Sc σ_C and N $2p_y$ are coupled into a triplet. A MCSCF function of this form, which allows for both states along the adiabatic potential curve, provides the structural correlation of both bonds, correlates for the $4s^2$–$4p^2$ near-degeneracy, and includes all possible spin couplings among the six valence electrons consistent with the desired spin state. The MCSCF wave function consists of 35 CSFs and dissociates properly to the sum of the $4s^2$–$4p^2$-correlated four-configuration MCSCF function for the Sc atom and the single SCF configuration function for the N atom [Sc(^{2}D) and N(^{4}S)].

The potential curves for all three levels of theory are shown in Figure 14 for the $^3\Pi$ state. Again the bond lengths are similar for all levels of theory. The repulsive part at intermediate bond distances due to the $4s^2$ interaction in the MCSCF curve is, again, not shown in the MCSCF(N2S)+1+2 and MCSCF+1+2 curves.

Computational Results. For a given species the inclusion of correlation results in a substantial increase in the calculated D_e, but the D_e's decrease slightly when the N 2s is opened up for correlation, since the N is 2s–2p hybridized. For the most part Figure 2 shows the same order of states at all three levels of theory. CI adds 30 kcal/mol to the dissociation energies of the doubly bonded species (and the triply bonded species with its weak σ bond) and 20 kcal/mol to the singly bonded species (and the σ,π doubly bonded $^3B_1$ state with its weak σ bond). The bond lengths at the MCSCF level of calculation are similar to that at the MCSCF+1+2 and MCSCF(N2S)+1+2 levels. The calculated vibrational frequencies are very sensitive to the level of calculation, but the MCSCF(N2S)+1+2 calculations give nearly the same frequency results as the MCSCF+1+2 calculation.

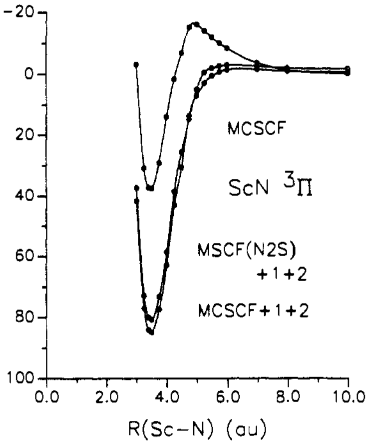

Figure 14. Potential energy curves for the σ,π doubly bonded $^3\Pi$ state of ScN as a function of internuclear separation for the MCSCF, MCSCF+1+2, and MCSCF(N2S)+1+2 calculations relative to the ground-state atoms. D_e, millihartrees.

VI. Conclusion

The electronic and geometric structures of 15 scandium nitride species with formal σ,π,π triple, σ,π double, $\pi\pi$ double, σ single, and π single two-electron bonds have been studied by ab initio MCSCF and multireference CI techniques and demonstrate the complexity of transition-element–main-group bonding due to the large number of low-lying excited states of the transition element. These calculations permit the following conclusions:

1. All 15 ScN states studied are bound with respect to the ground-state atoms. The ground-state ScN is the triply bonded $^1\Sigma^+$ with a bond energy of 62.7 kcal/mol (relative to the ground-state $4s^23d^1$ ^{2}D of Sc) and a bond length of 1.769 Å. It has an in situ $3d^3$ configuration and dissociates to the excited $4s^13d^2$ configuration of Sc.

2. Unlike bonding with main-group elements, the contributions of the π bonds to the bond strength can be equal to or greater than the contributions of the σ bonds, i.e., the σ bonds are weak and can be very weak. For instance: (a) The π,π doubly bonded $^3\Sigma^+$ state is 4.7 kcal/mol more stable than the σ,π doubly bonded $^3\Pi$. The bond energies of the various σ singly and π singly bonded species are similar and vary due to other factors than σ or π. (b) Breaking the σ bond in the triply bonded ground-state $^1\Sigma^+$ or in the σ,π doubly bonded $^3B_1$ to produce the π,π doubly bonded $^3\Sigma^+$ state or the σ,π doubly bonded $^5B_1$ state, respectively, costs only 7.4 and 4.1 kcal/mol, respectively, and does not change the bond lengths. Thus the σ bond is these species is very weak. This is an energetic compromise between using the Sc 4s for bonding, thereby lengthening the bond and destabilizing the π bonds, and using the $3d\sigma$ for bonding, thereby destabilizing the molecule since the states of the $3d^3$ configuration of Sc are so high in energy.

3. Within the context of these calculations, we expect that the σ bond of the ground-state triply bonded $^1\Sigma^+$ ScN will readily be broken by singly bonded R–R′ species, resulting in species with a linear RMNR framework with π,π doubly bonded Sc–N and σ singly bonded Sc–R and N–R. Indeed, we calculate that the reaction of ground-state $^1\Sigma^+$ ScN with molecular hydrogen to give linear $^1\Sigma^+$ HScNH is exothermic by 53.6 kcal/mol at the MCSCF level.

4. A comparison of bond energies and bond lengths, excluding that of the two species with the extremely weak σ bonds ($^1\Sigma^+$ and $^3B_1$), demonstrates the following: (a) For the species with an in situ $4s^13d^2$ Sc the bond energies of the σ,π and π,π doubly bonded species ($^3\Pi$ or $^3\Sigma^+$) are similar and roughly twice that of the most stable of the σ and π singly bonded species and that of the π,π doubly bonded species ($^3\Delta$) with an in situ $3d^3$ Sc. (b) The bond length decreases with increasing bond order, regardless of which orbitals are used for the formal bonds. The bond lengths of the σ,π and π,π doubly bonded species are similar and are shorter

than the bond lengths of the σ and π singly bonded species. (c) The spatial extent of the occupied orbitals along the bond axis contributes to the determination of the bond lengths. The bond length of the σ,π doubly bonded species is slightly longer than that of the π,π doubly bonded species. the σ singly bonded ScN species with an in situ excited-state Sc have remarkably constant bond lengths, which are slightly longer than the bond lengths of the π singly bonded species and the σ singly bonded $^3\Sigma^-$ state with an in situ ground-state $4s^23d^1$ Sc. (d) Nonbonded intraatomic spin couplings, whether high or low spin, do not affect the bond length and affect the bond energy slightly consistent with Hund's rules. However, high-spin repulsions between adjacent nonbonded Sc and N orbitals are quite strong and lengthen the bond slightly and decrease the bond energy by at least 10 kcal/mol.

5. The atomic populations show the following: (a) Bonding in all states has significant ionic Sc^+N^- character due to charge transfer from Sc to N. (b) Most importantly, the gross Sc to N charge transfer as a function of internuclear distance corresponds to a maximum at the equilibrium bond distance. (c) Despite different numbers of formal bonds, the gross Sc to N charge transfer is constant ($\sim$0.62) for all 14 nitrides studied with an in situ excited-state Sc configuration at equilibrium and greater than the $^3\Sigma^-$ state (0.48) with an in situ ground-state Sc. This appears to depend only on the properties of the in situ Sc configuration and the nitrogen electron affinity. (d) The Sc has 4s–3d mixing and the N is 2s–2p hybridized in all states.

6. The dipole moments of all 15 ScN states studied are large. Thus, we expect that an electron could easily add to form a ScN −1 anion. The dipole moment of the $^1\Sigma^+$ ground state varies dramatically near equilibrium concomitant with the change in character of the Sc σ bonding orbital.

7. We emphasized the structure of the ab initio MCSCF and multireference CI calculations that we have been using for transition-metal-containing species. The MCSCF wave functions include the essential physics, i.e., accounts for the strong intraatomic spin couplings on the transition element and the large $4s^2$–$4p^2$ near-degeneracy of the $4s^23d^1$ 2D ground-state Sc. The MCSCF potential curves follow the CI curves, resulting in similar bond lengths. The calculations are essentually size consistent at all theoretical levels.

Acknowledgment. We are indebted to the Argonne National Laboratory Theoretical Chemistry Group for providing the QUEST-164 electronic structure codes used in this study. This work was supported in part by the National Science Foundation (Grant CHE8519752).

Appendix. General Computational Details

Basis Sets. The basis set for Sc is the same as we have been using for Sc^+ and has been described previously.[2] It consists of 14s,11p,6d primitive Gaussian functions constructed by augmenting Wachters'[15] 14s,9p,5d basis with two additional diffuse p functions[16] and an extra d as recommended by Hay.[17] The Sc functions were contracted to 5s,4p,3d by using the method for generalized contraction of Raffenetti.[18] The basis sets for nitrogen and hydrogen were devised by Almlof and Taylor.[19]

Molecular Codes. All molecular calculations were done on a FPS-164 jointly supported by the Michigan State University Chemistry Department and the Office of the Provost, using the Argonne National Laboratory collection of QUEST-164 codes. In particular, the integrals were calculated with the program ARGOS written by Pitzer;[20] the SCF and GVB calculations used the GVB164 program by Bair;[21] the SCF and MCSCF final calculations used the UEXP program and related utility codes written by Shepard.[22] The configuration interaction calculations were done with the program UCI (and its related utility codes) written by Lischka, Shepard, Brown, and Shavitt.[23] The densities and the dipole moments were calculated by using locally written codes.

Spectroscopic Constants. Spectroscopic constants are obtained from the potential curves by means of Dunham analysis.[24] A fourth-order polynomial, fitted to five points around the minimum, was used to determine equilibrium bond length and vibrational frequency (Table I) at the various theoretical levels, and other spectroscopic constants at the MCSCF+1+2 level (Table II) (rotational constant, vibrational frequencies, centrifugal distortion constant, vibration–rotation interaction constant, and first anharmonicity constants).

MCSCF Wave Function and Dynamical Correlation. The structures of the bond dissociation energy calculations are illustrated in the body of the paper. The construction of the wave function for the $^1\Sigma^+$, $^3\Sigma^+$, $^3\Sigma^-$, and $^3\Pi$ states was described earlier and that for each of the remaining ScN states and for HScNH studied is described below. Each ScN MCSCF function is constructed and solved variationally as a function of the Sc–N separation. For those states correlating with an excited-state Sc atom it dissociates properly to the sum of the single self-consistent-field (SCF) configuration functions for the fragments in their correct spin state (the molecular asymptote). For those states correlating with the ground-state Sc it dissociates properly to the sum of the four-configuration MCSCF function for Sc and the single SCF configuration function for the N, both in their correct spin state. The HScNH MCSCF function is constructed and solved variationally in order to optimize the H–Sc, Sc–N, and N–H bond distances with a quadratic three-dimensional fit.

Computational Results. For each molecule discussed the number of spin eigenfunctions or configuration-state functions (CSF)[24] in C_{2v} symmetry for the various theoretical levels is tabulated in Table VI. For each theoretical level used the molecular absolute energies at the equilibrium internuclear distances and for eight states at an internuclear distance of 20.0 au are collected in Table VII. The corresponding atomic absolute energies are collected in Table VIII. These data show that all procedures dissociate properly in a size-consistent manner to within a millihartree.

$^1\Sigma^+$ Linear HScNH with Sc–N π,π Double Bond. The linear HScNH molecule formed by the addition of two hydrogen atoms to the unpaired electrons of the $^3\Sigma^+$-state ScN diradical has $^1\Sigma^+$ symmetry ($^1A_1$ under C_{2v} symmetry). Since for the $^3\Sigma^+$ ScN we find π,π double bond overwhelmingly dominant at equilibrium, only the π,π double bonded description is included here. The asymptotic form of the GVB representation of the wave function for the $^1\Sigma^+$ is as follows:

$$\begin{aligned} {}^1\Sigma^+\ ({}^1A_1) \sim {} & [\pi_y(Sc)\pi_y(N) + \pi_y(N)\pi_y(Sc)] \times \\ & [\pi_x(Sc)\pi_x(N) + \pi_x(N)\pi_x(Sc)][\sigma(Sc)\sigma(H_1) + \\ & \sigma(H_1)\sigma(Sc)][\sigma(N)\sigma(H_2) + \sigma(H_2)\sigma(N)] \end{aligned}$$

where the four spin pairs are (1) $\pi_y(Sc)$ and $\pi_y(N)$, (2) $\pi_x(Sc)$ and $\pi_x(N)$, (3) $\sigma(Sc)$ and $\sigma(H_1)$, and (4) $\sigma(N)$ and $\sigma(H_2)$; at the asymptote the $\sigma(Sc)$ is the Sc 4s and $\sigma(N)$ is the N $2p\sigma$. The MCSCF function of this form provides the structural correlation of the bonds in the GVB fashion and includes all possible spin coupling among the eight valence electrons consistent with the desired singlet spin state. It consists of 150 CSFs and separates to the SCF products in their correct spin state $[Sc((^2/_3)^{1/2}|z^4F\rangle - (^1/_3)^{1/2}|z^4D\rangle) + N(^4S) + H_1(^1S) + H_2(^1S)]$, where Sc has the $4s^14p\pi_x{}^1d\pi_y{}^1$ configuration. The MCSCF wave function is constructed and solved variationally as a function of the bond distances. Twelve points near the equilibrium were fit to a three-dimentional quadratic surface to optimize the bond lengths and determine the energy at equilibrium. The equilibrium energy is −815.45093 hartree.

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