5016 *J. Phys. Chem. A* **2004,** *108,* 5016−5025

Spin−Orbit Effects in the Ground States of Singly Positive and Neutral V_2, VNb, and Nb_2: INDO/S and Empirical Model Calculations

Ted A. O'Brien[†]

Quantum Theory Project, University of Florida, P.O. Box 118435, Gainesville, Florida 32611, and Chemistry Department, Indiana University, 800 East Kirkwood Avenue, Bloomington, Indiana 47405

Received: November 8, 2001; In Final Form: February 5, 2004

Ground-state spin−orbit splittings in V_2^+, VNb^+, and Nb_2^+ were investigated with spin−orbit configuration interaction (SOCI) calculations using the intermediate neglect of differential overlap method for optical spectroscopy (INDO/S). Splittings found for the $X^4\Sigma^-$ ground states of V_2^+ and VNb^+ using a CI treatment isolating essential correlation of the ground and isoconfigurational $a^2\Sigma^+$ and $b^2\Sigma^-$ state wave functions agreed well with experiment. The size of the splitting for Nb_2^+ was predicted. In all three cases the $a^2\Sigma^+$ and $b^2\Sigma^-$ states were found to be strongly coupled by the spin−orbit operator. Several perturbative models for predicting energies of interacting excited states based on measured splittings were analyzed by comparing to SOCI results for V_2, VNb, and Nb_2. Second-order perturbation theory, treating only the isoconfigurational states, and neglecting overlap and CI in computing couplings was the best choice of approximations due to cancellation of errors. An empirical model treating the isoconfigurational states of the cations was developed within these guidelines and agrees well with SOCI calculations for V_2^+. The empirical wave functions were divergent for Nb_2^+ due to similar energies of the doublet states. Analysis of correlation effects in the INDO/S model indicates that a charge-iterative method could be effective for systematically correlated semiempirical calculations on metal cluster ions.

I. Introduction

Transition metal clusters are an area of active research because of their relevance to heterogeneous catalysis, but there are some major difficulties associated with their investigation. One important problem lies in preparation and characterization, as bare clusters tend to be highly refractory. Second, application of theoretical methods to metal clusters is not straightforward due to the severity of the electron correlation problem for these molecules. Even the diatomics remain a challenge for accurate ab initio methods, and detailed application of highly correlated calculations to clusters larger than just a few atoms is often impractical. This is unfortunate because clusters of even slightly larger size are of vital interest as examples of states of matter intermediate between molecules and bulk aggregates,[1] and as models of metal surfaces.

Clusters of intermediate size are potentially within reach of efficient semiempirical methods (recent calculations were reported on nickel clusters of up to 51 atoms in size[2]), but special problems are posed by the rather ad hoc treatment of correlation effects in semiempirical calculations. In these methods, dynamic correlation is thought to be incorporated in an average, unsystematic way—a scenario suggested on the basis of the ab initio effective valence shell Hamiltonian[3−14] rather than an examination of working semiempirical models. An in-depth understanding of the nature of correlation effects in the models themselves will be necessary if the methods are to be rationally applied to transition metal clusters. Recent spin−orbit enhanced configuration interaction (SOCI) calculations on the neutral diatomics V_2, VNb, and Nb_2 using the intermediate neglect of differential overlap Hamiltonian parametrized for optical spectroscopy (INDO/S) showed promise that this method can be successful with these molecules as long as correlation is handled carefully.[15,16] This paper extends that work to the cations V_2^+, VNb^+, and Nb_2^+ and examines several outstanding issues left by previous work on the neutral molecules.

The ground states of V_2, VNb, and Nb_2 have unusually large spin−orbit splittings,[15−20] 75 cm^{-1} for V_2,[17] 230 cm^{-1} for VNb,[18] and 410 cm^{-1} for Nb_2.[21] (These experimentally determined splittings are henceforth referred to as Δ.) All three molecules have $X^3\Sigma^-$ ground states with valence electron configuration $(d\pi_u)^4(1\sigma_g)^2(2\sigma_g)^2(\delta_g)^2$, as established by both experimental[17−20,22−24] and theoretical[15,16,25−31] investigations. The splitting has been attributed to second-order spin−orbit interaction of the $\Omega'' = 0$ component of the ground state with the isoconfigurational $^1\Sigma^+$ state (henceforth referred to as $a^1\Sigma^+$) in each case.[15−19,22] The splittings are large because the $a^1\Sigma_g^+$ state has a very low energy, as is often the case with transition metal clusters due to near degeneracy and orbital localization effects.[30,32]

Several electronic transitions to excited states have been observed for V_2 and Nb_2 as well. Empirical models for predicting the energies of the interacting $a^1\Sigma_g^+$ states have been proposed[18,22,24] and used to assign some of the transitions. In these empirical models, an approach such as second-order perturbation theory is used to treat the interaction of the two states, with their spin−orbit matrix element taken as a linear combination of atomic spin−orbit radial integrals. The resulting expression for the perturbation of the ground state is set equal to the experimental value of Δ, and rearrangement yields an expression for the excited-state energy. Estimates of 1821 [22] and 1196 cm^{-1} [18] have been made for the energy of the $a^1\Sigma_g^+$ state of V_2, depending on how the coupling matrix element is calculated. On the basis of the former, an excited state observed at 1860 cm^{-1} in matrix isolated resonance Raman work[33] was assigned as $a^1\Sigma_g^+$ [22] (the spin selection rule was assumed to be

---

[†] Present address: Department of Chemistry, Indiana University−Purdue University Indianapolis, Indianapolis, IN 46202.

10.1021/jp014108s CCC: $27.50

relaxed due to triplet contamination of the excited singlet state). A similar situation holds for Nb_2, where the energy of the interacting $a^1\Sigma_g^+$ state has been empirically estimated as 2375 [18] or 2834 cm^{-1},[19] and a resonance Raman transition has been observed at 2445 cm^{-1}.[34]

Several theoretical investigations on V_2 and Nb_2 have been reported.[15,16,25−31] Semiempirical spin−orbit enhanced configuration interaction (SOCI) calculations using the INDO/S model on V_2 showed close agreement with $\Delta = 75$ cm^{-1} and the empirical prediction of 1196 cm^{-1} for $E(a^1\Sigma_g^+)$. These results cast doubt on the assignment of the state observed at 1860 cm^{-1} as $a^1\Sigma_g^+$. In the case of Nb_2, however, both INDO/S SOCI calculations[16] and empirical models give $E(a^1\Sigma_g^+)$ in reasonable agreement with the observed transition energy (2445 cm^{-1}). The calculations did not indicate the presence of any other low-lying states for the two molecules. It is thus difficult to distinguish between the two hypotheses, that the excited states observed for V_2 and Nb_2 are the $a^1\Sigma_g^+$ states, or are some other low-lying state the molecules have in common.

More recent complete active space self-consistent field calculations followed by multireference configuration interaction (CASSCF/MRCI, ref 35) on Nb_2 did not help clarify the situation. Δ was estimated as 500−1000 cm^{-1} (experiment 410 cm^{-1} [21]) and $E(a^1\Sigma_g^+)$ as 787−1545 cm^{-1} depending on the level of calculation. The CASSCF/MRCI results do not provide a strong possibility for a low-lying state other than the $a^1\Sigma_g^+$ state that could account for the observed transition. Further experimental and theoretical work is needed to elucidate this question.

The cations V_2^+, VNb^+, and Nb_2^+ have $X^4\Sigma^-$ ground states with $(d\pi_u)^4(1\sigma_g)^2(2\sigma_g)^1(\delta_g)^2$ valence configurations.[18,20,27] In these cases, it has been suggested that spin−orbit interaction between the $\Omega = \pm^1/_2$ components of the isoconfigurational $X^4\Sigma^-$ and $^2\Sigma^+$ (henceforth $a^2\Sigma^+$) states causes the splitting of the ground state,[18] measured as $\Delta = 20$ [18] and 21 cm^{-1} [20] for V_2^+ and 82 cm^{-1} for VNb^+.[18] Δ has not been measured for Nb_2^+ but was estimated to be 142 cm^{-1} using unperturbed state energies determined with density functional theory.[27] A theoretical prediction made with explicit consideration of spin−orbit coupling has not been presented, however.

The spin−orbit effects observed for the ground states of the cations could provide a useful analogy for the neutral molecules, but there is less experimental evidence available about the interacting excited states. The energies of the $a^2\Sigma^+$ states in V_2^+ and VNb^+ were predicted with the empirical model using the experimentally determined splittings of the $X^4\Sigma^-$ states.[18] There is also a third isoconfigurational state for a $(d\pi_u)^4(1\sigma_g)^2(2\sigma_g)^1(\delta_g)^2$ configuration, referred to here as $b^2\Sigma^-$, which was presumed to play no role in ref 18. CASSCF/MRCI calculations on Nb_2^+ confirmed that the ground state is $X^4\Sigma_g^-$ and provided some predictions about the energies of the various excited states. These are compared with the results of INDO/S SOCI calculations below.

Initially it was expected that INDO/S calculations on the cations would be similar to the earlier efforts with the neutrals,[16] giving reasonable agreement with the empirical predictions and CASSCF calculations,[35] but certain discrepancies were found. These included larger disagreement between empirical and INDO/S energies than found for the neutrals, and quartet contamination of both excited doublet states. This unexpected outcome motivated a more detailed investigation of the two-state empirical models. In the case of the cations it was discovered that there is a significant coupling between the $a^2\Sigma^+$ and $b^2\Sigma^-$ states that was neglected in ref 18. This coupling can be quite large because the two states have similar energies. A new empirical model incorporating the doublet−doublet interaction was designed by reexamining the empirical calculations on the neutral molecules. This also allowed a systematic examination of the effect of the various approximations used, which has not been made previously even though these models are often applied to metal clusters (e.g., see refs 36 and 37).

In summary, this paper presents results of INDO/S SCF/SOCI calculations on V_2^+, VNb^+, and Nb_2^+, along with a new empirical model describing isoconfigurational spin−orbit effects in the cations that includes coupling between the $a^2\Sigma^+$ and $b^2\Sigma^-$ states. An analysis of the various approximations employed in previous empirical models has also been made. The paper is organized as follows. Section II describes the methods of calculation used, including the INDO/S SOCI calculations and the empirical models. Section III provides presentation and discussion of results, including comparisons between results found with INDO/S and experiment for the cations and neutrals, as well as with various realizations of the empirical models. Conclusions are summarized in the fourth and final section.

II. Methods

A. INDO/S SOCI Method. The SOCI calculations on V_2^+, VNb^+, and Nb_2^+ were performed using the INDO/S model[38−41] implemented in the ZINDO software package.[42] The calculations consist of three steps: a self-consistent field molecular orbital calculation, a configuration interaction calculation in a basis of spin-adapted configuration state functions constructed using the SCF MOs, and the final spin−orbit calculation involving matrix diagonalization in a basis of components of CI states of multiplicities linked by the spin−orbit operator. A brief description of each step follows.

Self-consistent field molecular orbitals are obtained in a valence orbital basis set consisting of the nine valence ns, np, and $(n - 1)$d orbitals on each atom. Following previous work,[15,16] SCF calculations were performed using either the configuration-averaged Hartree−Fock (CAHF, ref 43) or restricted open shell Hartree−Fock (ROHF, ref 44) procedure. Two ROHF formulations were used, in which the SCF orbitals are partitioined into a closed shell part and one or more sets of open shell orbitals. The SCF energy is expressed as

$$E_{\mathrm{ROHF}} = 2\sum_i h_i + \sum_{i<j}(2J_{ij} - K_{ij}) + \frac{1}{2}\sum_{i,m} n_m(2J_{im} - K_{im}) + \sum_m n_m h_m + \frac{1}{4}\sum_\mu\sum_\nu\sum_{m\in\mu}\sum_{p\in\nu} n_m n_p(2a^{\mu\nu}J_{mp} - b^{\mu\nu}K_{mp}) \quad (1)$$

where i, j, etc. represent closed shell orbitals; m, p, etc. represent open-shell orbitals; n_m is the number of electrons in orbital m; h_α, $J_{\alpha\beta}$, and $K_{\alpha\beta}$ are the usual one-electron, Coulomb, and exchange integrals, respectively; μ, ν, etc. represent open shells (i.e., separate groups of open shell orbitals); and $a^{\mu\nu}$ and $b^{\mu\nu}$ are the "vector coupling coefficients" that couple the open shell electrons. The choice of vector coupling coefficients fixes the configuration or average over configurations used in the calculation. In the standard ROHF definition, there is one open shell containing the 2σ and δ_g MOs, each occupied by an α-spin electron., and $\mu = \nu = 1$, $a = 1$, $b = 2$. A second ROHF ground state was defined with two separate open shells. The first included the 1σ and 2σ MOs with coupling coefficients representing an average over configurations $1\sigma^2 2\sigma^1$ and $1\sigma^1 2\sigma^2$, and the second consisted of the δ_g MOs with single occupancy. The coupling coefficients for this case are $a^{11} = 8/9 = b^{11}$, $a^{12} = 1$, $b^{12} = 4/3$, $a^{22} = 1$, $b^{22} = 2$. This second nonstandard definition was used for VNb^+ due to SCF convergence problems (vide infra).

Once a set of self-consistent field MOs has been obtained, configuration interaction (CI) calculations are carried out for states of multiplicities linked by the spin−orbit operator. In the case of the cations with $^4\Sigma^-$ ground states, then, this would typically include doublets and sextets in addition to quartets. Spin-adapted configuration-state functions (CSFs) are obtained using a Rumer diagram technique.[45,46] The resulting nonorthogonal valence bond structures are orthogonalized using the Schmidt procedure prior to diagonalization of the CI matrix.[16] In an additional step, matrix elements of the spin−orbit operator (taken as an effective one electron operator) in the basis of components of the CI states are computed using only one-center terms and empirical values for spin−orbit radial integrals.[47] The resulting matrix ($\mathbf{H} + \mathbf{H}^{\mathrm{S.O.}}$) is diagonalized to yield the spectroscopic levels,[48] and transition probabilities between selected levels are calculated assuming the dipole length approximation.[47]

The bond length of V_2^+ was set equal to the value of r_0 determined experimentally,[20] 1.735 Å. In contrast to the neutral diatomics, where bond lengths have been determined experimentally for V_2,[17] VNb,[23] and Nb_2,[19] bond lengths for VNb^+ and Nb_2^+ have not been determined experimentally. Values predicted by DFT calculations on the cations[27] are used here, 1.885 and 2.044 Å, respectively. These are likely good estimates, because the bond length predicted by the DFT calculations for V_2^+ (1.741 Å) agreed with the experimental value (1.735 Å), and similar calculations[19] yielded bond distances of 1.777 Å for V_2 (experiment 1.766 Å[17]) and 2.08 Å for Nb_2 (2.078 Å[19]). The DFT value of 2.044 Å for Nb_2^+ is adopted rather than the value of 2.151 Å found with CASSCF/MRCI calculations[35] because the bond length of Nb_2 predicted by these calculations was ~0.10 Å too long, whereas the DFT calculations estimated this bond length to within 0.002 Å of experiment.[19]

B. Empirical Models for Neutral Molecules. In this section empirical equations similar to those used previously[18,22] are developed to predict the energy of the perturbing $a^1\Sigma^+$ state for the neutral molecules. A particular goal is to investigate the various approximations involved in these models. The most effective combination found for V_2, VNb, and Nb_2 by comparing to the more accurate INDO/S SOCI results[16] will then be applied to the cations. This investigation is of general interest, as empirical models of this sort are often used for predicting state energies for metal clusters.[36,37]

The basic strategy of these models is the reverse of the typical application of perturbation theory, because the size of the perturbation is known from experiment (Δ). Because the couplings can be approximated, the difference in unperturbed energies of the ground state and interacting state can be found. Adding the perturbations of the ground and excited states then gives the perturbed energy of the excited state. There are three important approximations made in this procedure, including neglect of orbital overlap and CI in determining coupling matrix elements, order at which the perturbation of spin−orbit coupling is treated, and inclusion of only two states in the model. Each of these is considered below.

1. Evaluation of Coupling Matrix Element with Overlap. Two related approximations were made in previous derivations.[18,22] The first is neglect of overlap integrals in evaluating spin−orbit matrix elements, which omits terms proportional to $\zeta_{(n-1)\mathrm{d}}S$, where S is the delta-symmetry overlap integral. The second is neglect of the extensive CI of the $(\mathrm{d}\pi_u)^4(\mathrm{d}\sigma_g)^2(\mathrm{s}\sigma_g)^2(\mathrm{d}\delta_g)^2$ and $(\mathrm{d}\pi_u)^4(\mathrm{d}\sigma_g)^2(\mathrm{s}\sigma_g)^2(\mathrm{d}\delta_u)^2$ configurations, which is known to be large for V_2 and Nb_2.[15,16,29,30,35] This CI imparts local character to the delocalized MO description of the δ_g orbitals. It was previously assumed that the δ_g MOs are completely local,[18,22] but this is only partially true for these molecules. Even though the two configurations are not coupled by the one-electron operator $\hat{H}^{\mathrm{S.O.}}$, the CI does indirectly affect the matrix element when overlap is retained. Because the amount of CI is itself also related to the overlap (greater CI occurs as the overlap gets smaller), the two approximations just described are together referred to as "neglect of overlap" throughout this paper.

The coupling matrix element $\langle X^3\Sigma^-(0^+)|\hat{H}^{\mathrm{S.O.}}|a^1\Sigma^+(0^+)\rangle$ developed here includes both overlap integrals and CI between the configurations with open-shell occupancies $\mathrm{d}\delta_g^2$ and $\mathrm{d}\delta_u^2$. Spin-adapted linear combinations of Slater determinants representing the $\Omega = 0$ components of Σ symmetry are

$$^3\Phi_0 = \frac{1}{\sqrt{2}}(|\delta_g^+\alpha\delta_g^-\beta| + |\delta_g^+\beta\delta_g^-\alpha|) \tag{2}$$

$$^3\Phi_0' = \frac{1}{\sqrt{2}}(|\delta_u^+\alpha\delta_u^-\beta| + |\delta_u^+\beta\delta_u^-\alpha|) \tag{3}$$

$$^1\Phi_0 = \frac{1}{\sqrt{2}}(|\delta_g^+\alpha\delta_g^-\beta| - |\delta_g^+\beta\delta_g^-\alpha|) \tag{4}$$

$$^1\Phi_0' = \frac{1}{\sqrt{2}}(|\delta_u^+\alpha\delta_u^-\beta| - |\delta_u^+\beta\delta_u^-\alpha|) \tag{5}$$

Wave functions for the $X^3\Sigma^-(0^+)$and $^1\Sigma^+(0^+)$ components are then

$$\Psi(X^3\Sigma^-(0^+)) = {^3C_1}{^3\Phi_0} + {^3C_2}{^3\Phi_0'} \tag{6}$$

$$\Psi(^1\Sigma^+(0^+)) = {^1C_1}{^1\Phi_0} + {^1C_2}{^1\Phi_0'} \tag{7}$$

The coefficients can be readily obtained with a small CI calculation.

The spin−orbit coupling can be determined by expanding the Slater determinants in terms of the atomic orbitals that make up the molecular orbitals, and evaluating the resulting matrix elements. All matrix elements listed in this paper are derived using a more efficient procedure based on Rumer diagrams.[48,49] Two important assumptions are used in doing so. First, two-center radial integrals are neglected (a standard assumption[50]). Second, because the $X^3\Sigma^-$ and $a^1\Sigma^+$ states are isoconfigurational, it is reasonable to assume that the extent of localization is similar in the two states, and therefore $^3C_1 = {^1C_1} \equiv C_1$ and $^3C_2 = {^1C_2} \equiv C_2$. With these assumptions the coupling term is given by

$$\langle\Psi(X^3\Sigma^-(0^+))|\hat{H}^{\mathrm{S.O.}}|\Psi(^1\Sigma^+(0^+))\rangle = 2\bar{\zeta}(\mathrm{d})\left[\frac{{C_1}^2}{(1+S)} + \frac{{C_2}^2}{(1-S)}\right] \tag{8}$$

where $\bar{\zeta}_\mathrm{d}$ is $\zeta_{(n-1)\mathrm{d}}$ for V_2 and Nb_2, and the average of $\zeta_{3\mathrm{d}}$ and $\zeta_{4\mathrm{d}}$ in the case of VNb.[51] The values of $\zeta_{(n-1)\mathrm{d}}$ (145.0 cm^{-1} for vanadium and 448.8 cm^{-1} for niobium) are taken for the $ns^1(n-1)d^4$ configuration of each metal, which is the diabatic dissociation limit of the molecules. Equation 8 reduces to the previously used[18,22] value of $2\bar{\zeta}(\mathrm{d})$ when the overlap is zero but is more general because it is also applicable when S is nonzero. Because $|C_1|$ is greater than $|C_2|$ when S is nonzero and S is positive, inclusion of overlap reduces the magnitude of the coupling and thus decreases the estimate made for $E(a^1\Sigma^+)$.

2. Order of Perturbation Expansion. In second-order perturbation theory, the perturbation of the $\Omega'' = 0$ component of the ground state is

$$\Delta_1 = \sum_{i=2}^{n} \frac{{H_{1i}}^2}{E_1^{(0)} - E_i^{(0)}} \tag{9}$$

where $E_i^{(0)}$ is the unperturbed energy of the *i*th level, and H_{1i} is the spin−orbit coupling of the ground level and the *i*th excited level. The number of states considered in the model is *n*, limited to two in the previous treatments.[18,22] In the following discussion, it is assumed that the $i = 2$ level is the $a^1\Sigma_g^+(0_g^+)$ level. The perturbation of this level is given by

$$\Delta_2 = \sum_{i\neq 2}^{n} \frac{{H_{2i}}^2}{E_2^{(0)} - E_i^{(0)}} \tag{10}$$

If *n* is limited to two, Δ_1 and Δ_2 are equal in magnitude but opposite in sign:

$$\Delta = -\Delta_1 = \Delta_2 = \frac{{H_{12}}^2}{E_2^{(0)} - E_1^{(0)}} \tag{11}$$

Δ is therefore positive in sign because $E_2^{(0)} > E_1^{(0)}$. With these definitions, the energy of the excited level is then

$$E(a^1\Sigma^+) = E_2^{(0)} - E_1^{(0)} + 2\Delta = \frac{{H_{12}}^2 + 2\Delta^2}{\Delta} \tag{12}$$

An analogous expression that is correct through infinite order can be obtained by diagonalizing a 2 × 2 matrix.[52] The appropriate matrix equation is

$$\begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix}^{\dagger} \begin{bmatrix} E_1^{(0)} & H_{12} \\ H_{12} & E_2^{(0)} \end{bmatrix} \begin{bmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{bmatrix} = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \tag{13}$$

Solving by means of a secular determinant and rearranging leads to

$$E(a^1\Sigma^+) = E_2^{(0)} - E_1^{(0)} + 2\Delta = \frac{{H_{12}}^2 + \Delta^2}{\Delta} \tag{14}$$

(see ref 18 for a more detailed derivation of this), which is smaller than the second-order expression by Δ, the spin−orbit splitting of the ground state. Extension of the model to infinite order thus reduces the estimate of $E(a^1\Sigma_g^+)$ compared to the estimate made at second order.

It should be noted that different analytical expressions for Δ are implicitly assumed in eqs 12 and 14, but in each case Δ is substituted as an empirical parameter to solve for the excited-state energy. Though it seems apparent that the most exact expression should be used, this is not necessarily the case due to cancellation of errors caused by the other approximations (i.e., limitation to two states and neglect of overlap).

3. Limitation to Two States. It is more difficult to quantify the impact of including other states in the empirical model. Additional singlet states could interact with the $\Omega'' = 0$ level of the ground state, lowering its energy and thus increasing the ground-state splitting. Similarly, additional triplet states could interact with the $\Omega'' = \pm 1$ levels, lowering their energy and decreasing the splitting. The overall effect would then depend on the identities of the interacting states and their energies, which are unknown. If the additional interactions were primarily with singlet states, however, then their inclusion would increase the estimate of $E(a^1\Sigma_g^+)$. This is true because with two states, the model assumes that all of the perturbation of the $\Omega'' = 0$ level arises from interaction with the $a^1\Sigma_g^+$ state. If a part of the perturbation in caused by other states, however, the perturbation caused by the $a^1\Sigma_g^+$ state is smaller than the observed splitting. Because the coupling between states is constant, a smaller perturbation can be obtained only by increasing the energy of the excited state.

Exactly this situation was found previously for Nb_2, in which the INDO/S SOCI eigenvector for the $\Omega'' = 0$ component of $X^3\Sigma_g^-$ was found to be contaminated by several singlet CSFs other than those representing the $a^1\Sigma_g^+$ state.[16] If the other molecules behave similarly, then including additional states should systematically increase the estimate for $E(a^1\Sigma_g^+)$. Because higher levels of perturbation theory and including overlap effects tend to decrease the estimate, the two-state model at second order with no CI or overlap could benefit from some cancellation of errors.

C. Empirical Model for Cations, Second-Order with No Overlap. For the cations the results of the next section, that the best choice of approximations is second-order perturbation theory with neglect of overlap effects, is anticipated, and the empirical model is developed accordingly. James et al.[18] have already considered this problem, assuming second-order spin−orbit interaction between the isoconfigurational $X^4\Sigma^-$ and $a^2\Sigma^+$ states. Their analysis is incomplete, however, because they neglected coupling between the isoconfigurational $a^2\Sigma^+$ and $b^2\Sigma^-$ states. Configuration-state functions for the three spin components are[50]

$$\Psi\left(X^4\Sigma^-\left(\frac{1}{2}\right)\right) = \frac{1}{\sqrt{3}}[|\sigma_g\alpha\delta_g^+\alpha\delta_g^-\beta\rangle + |\sigma_g\alpha\delta_g^+\beta\delta_g^-\alpha\rangle + |\sigma_g\beta\delta_g^+\alpha\delta_g^-\alpha\rangle] \tag{15}$$

$$\Psi\left(a^2\Sigma^+\left(\frac{1}{2}\right)\right) = \frac{1}{\sqrt{2}}[|\sigma_g\alpha\delta_g^+\alpha\delta_g^-\beta\rangle - |\sigma_g\alpha\delta_g^+\beta\delta_g^-\alpha\rangle] \tag{16}$$

$$\Psi\left(b^2\Sigma^-\left(\frac{1}{2}\right)\right) = \frac{1}{\sqrt{6}}[2|\sigma_g\beta\delta_g^+\alpha\delta_g^-\alpha\rangle - |\sigma_g\alpha\delta_g^+\alpha\delta_g^-\beta\rangle - |\sigma_g\alpha\delta_g^+\beta\delta_g{}^-\alpha\rangle] \tag{17}$$

CSFs for the $M_S = -^1/_2$ components are analogous to these, with the α and β spins exchanged, and have the same coupling interactions derived below for the $M_S = +^1/_2$ components.

Matrix elements between the CSFs are straightforwardly evaluated using the Rumer diagram method.[48,49] Under the assumption of zero δ symmetry overlap and neglecting two-center spin−orbit radial integrals, the matrix elements are

$$\left\langle X^4\Sigma^-\left(\pm\frac{1}{2}\right)\middle|\hat{H}^{S.O.}\middle|a^2\Sigma^+\left(\pm\frac{1}{2}\right)\right\rangle = \frac{4\bar{\zeta}_d}{\sqrt{6}} \tag{18}$$

$$\left\langle X^4\Sigma^-\left(\pm\frac{1}{2}\right)\middle|\hat{H}^{S.O.}\middle|b^2\Sigma^-\left(\pm\frac{1}{2}\right)\right\rangle = 0 \tag{19}$$

$$\left\langle a^2\Sigma^+\left(\pm\frac{1}{2}\right)\middle|\hat{H}^{S.O.}\middle|b^2\Sigma^-\left(\pm\frac{1}{2}\right)\right\rangle = -\frac{2\bar{\zeta}_d}{\sqrt{3}} = -\frac{1}{\sqrt{2}}\left\langle X^4\Sigma^-\left(\pm\frac{1}{2}\right)\middle|\hat{H}^{S.O.}\middle|a^2\Sigma^+\left(\pm\frac{1}{2}\right)\right\rangle \tag{20}$$

Here $\bar{\zeta}_d$ is again taken as the average of $\zeta_{(n-1)d}$ for configurations corresponding to the diabatic dissociation products of the cations. The values are as follows: for V_2^+, [Ar]$4s^13d^4$, $\zeta_{3d} = 145.0$ cm^{-1} and [Ar]$3d^4$, $\zeta_{3d} = 172.5$ cm^{-1}; for VNb$^+$, [Ar]$3d^4$, $\zeta_{3d} = 172.5$ cm^{-1} and [Kr]$5s^14d^4$, $\zeta_{4d} = 448.8$ cm^{-1}; for Nb_2^+, [Kr]$4d^4$, $\zeta_{4d} = 479.1$ cm^{-1} and [Kr]$5s^14d^4$, $\zeta_{4d} = 448.8$ cm^{-1}. Equation 18 agrees with the previous development of James et al.[18]

In evaluating interactions between the states at second order, the following definitions and equalities are assumed:

$$|\psi_1^{(0)}\rangle = X^4\Sigma^- \qquad |\psi_2^{(0)}\rangle = a^2\Sigma^+ \qquad |\psi_3^{(0)}\rangle = b^2\Sigma^-$$

$$H_{12} = \frac{4\bar{\zeta}_d}{\sqrt{6}} \qquad H_{13} = 0 \qquad H_{23} = -\frac{1}{\sqrt{2}}H_{12}$$

$$E_1^{(0)} = 0 \qquad E_1^{(2)} = -\Delta \qquad E_3^{(0)} = E_2^{(0)} + \Delta E \quad (21)$$

where Δ is the experimentally determined splitting of the $X^4\Sigma^-$ state, and ΔE is the difference in the unperturbed energies of the $b^2\Sigma^-$ and $a^2\Sigma^+$ states, $\Delta E = E^{(0)}(b^2\Sigma^-) - E^{(0)}(a^2\Sigma^+)$. With these assumptions the following equations are obtained:

$$\Delta = -\Delta_1 = \frac{{H_{12}}^2}{E_2^{(0)} - E_1^{(0)}} \quad (22)$$

$$E_2^{(2)} = \frac{{H_{12}}^2}{E_2^{(0)} - E_1^{(0)}} + \frac{{H_{23}}^2}{E_2^{(0)} - {E_3}^{(0)}} = \frac{{H_{12}}^2}{E_2^{(0)} - E_1^{(0)}} - \frac{1}{2}\frac{{H_{12}}^2}{\Delta E} \quad (23)$$

$$E_3^{(2)} = \frac{{H_{23}}^2}{E_3^{(0)} - E_2^{(0)}} = \frac{1}{2}\frac{{H_{12}}^2}{\Delta E} \quad (24)$$

Using $E_i = E_i^{(0)} + E_i^{(2)}$, making substitutions of eqs 21, rearranging, and taking the appropriate subtractions gives

$$E(a^2\Sigma^+) - E(X^4\Sigma^-) = \frac{{H_{12}}^2 + 2\Delta^2}{\Delta} - \frac{1}{2}\frac{{H_{12}}^2}{\Delta E} \quad (25)$$

$$E(b^2\Sigma^-) - E(X^4\Sigma^-) = \frac{{H_{12}}^2 + \Delta^2}{\Delta} + \frac{1}{2}\left(\frac{{H_{12}}^2 + 2(\Delta E)^2}{\Delta E}\right) \quad (26)$$

Equation 25 can be compared to eq 12, which is valid in the case of two coupled states. The coupling between the excited states thus changes the energy of the $a^2\Sigma^+$ state according to the second term on the right side of eq 25.

Equations 25 and 26 require an additional parameter, ΔE, the difference in unperturbed energies of the $a^2\Sigma^+$ and $b^2\Sigma^-$ states. This difference can be obtained from empirical fits to atomic energy levels. Using eqs 16 and 17 and the Condon–Slater rules[52] for evaluating matrix elements between Slater determinants, ΔE is given by

$$\Delta E = E^{(0)}(b^2\Sigma^-) - E^{(0)}(a^2\Sigma^+) = 2(K_{\sigma\delta^+} - K_{\delta^+\delta^-}) \quad (27)$$

where K_{ab} is the exchange integral $\langle ab|ba\rangle$, and the fact that $K_{\sigma\delta^+} = K_{\sigma\delta^-}$ has been used. In each case, the molecular exchange integrals are expanded over the atomic basis set. Under the INDO approximation.[53] Equation 27 reduces to

$$\Delta E = \langle\chi^\sigma\chi^+|\chi^+\chi^\sigma\rangle - \langle\chi^+\chi^-|\chi^-\chi^+\rangle \quad (28)$$

for the homonuclear case, where χ^σ is an atomic orbital of σ symmetry (either $(n-1)d_{z^2}$ or ns), and χ^+ and χ^- are d orbitals of δ symmetry. In the case of VNb$^+$, these integrals are replaced by averages of the integrals for each element.[51] Equation 28 can be expressed in terms of the Slater–Condon factors,[54] which have been fit empirically to atomic energy levels for the 3d metals.[55] Two cases are considered, in which the open-shell σ bonding MO is sσ in character or dσ in character. With the appropriate substitutions (see ref 40) eq 28 becomes

$$\Delta E(s\sigma^1 d\delta^2) = \frac{1}{5}G^2(sd) - \frac{35}{441}F^4(dd) \quad (29)$$

$$\Delta E(d\sigma^1 d\delta^2) = \frac{4}{49}F^2(dd) - \frac{20}{441}F^4(dd) \quad (30)$$

An alternative approach would be to obtain the molecular exchange integrals directly from an SCF calculation, but proceeding in this fashion would sacrifice the empirical aspect of the treatment.

Care must be exercised in selecting values for the Slater–Condon integrals of eqs 29 and 30 because their values depend on charge. For vanadium, for example, different values of G^2(sd) and F^4(dd) have been fit on the basis of atomic spectroscopy[55] for V, $3d^44s^1$ and V$^+$, $3d^4$. Here averages of these values are used, 26 650 cm^{-1} for F^4(dd) and 7090 cm^{-1} for G^2(sd). A careful fit of Slater–Condon integrals has not been performed for the 4d metals, but values for F^2(dd) and F^4(dd) can be extracted from the Racah parameters B and C.[56] Again there are different values for neutral and positive niobium, which give average values of 29 127 cm^{-1} for F^2(dd) and 27 733 cm^{-1} for F^4(dd).

A final point to consider is that the couplings of eqs 18–20 imply that both excited doublet states have partial quartet character. Though the $b^2\Sigma^-$ state does not mix directly with the quartet ground-state, spin–orbit mixing of the $a^2\Sigma^+$ and $b^2\Sigma^-$ states imparts some quartet character to the $b^2\Sigma^-$ state. This can be seen by considering the wave functions for each state correct through second order. Assuming intermediate normalization and eqs 21, the relevant expressions are[52]

$$|\Psi^{(2)}(X^4\Sigma^-)\rangle = |\Psi^{(0)}(X^4\Sigma^-)\rangle - \frac{\Delta}{H_{12}}|\Psi^{(0)}(a^2\Sigma^+)\rangle - \frac{1}{\sqrt{2}}\frac{\Delta^2}{{H_{12}}^2 + \Delta E\Delta}|\Psi^{(0)}(b^2\Sigma^-)\rangle \quad (31)$$

$$|\Psi^{(2)}(a^2\Sigma^+)\rangle = \frac{\Delta}{H_{12}}|\Psi^{(0)}(X^4\Sigma^-)\rangle + |\Psi^{(0)}(a^2\Sigma^+)\rangle + \frac{1}{\sqrt{2}}\frac{H_{12}}{\Delta E}|\Psi^{(0)}(b^2\Sigma^-)\rangle \quad (32)$$

$$|\Psi^{(2)}(b^2\Sigma^-)\rangle = -\frac{1}{\sqrt{2}}\frac{{H_{12}}^2\Delta}{\Delta E({H_{12}}^2 + \Delta E\Delta)}|\Psi^{(0)}(X^4\Sigma^-)\rangle - \frac{1}{\sqrt{2}}\frac{H_{12}}{\Delta E}|\Psi^{(0)}(a^2\Sigma^+)\rangle + |\Psi^{(0)}(b^2\Sigma^-)\rangle \quad (33)$$

The magnitude of the contribution of each zeroth-order wave function to these second-order wave functions can be found by dividing the square of the coefficient leading the zeroth-order function by the sum of the squares of all three coefficients.

The fact that both excited doublet states are spin-contaminated with quartet character is an important point, because spin contamination was invoked in assigning low-energy excited states observed for V_2 and Nb_2 as $a^1\Sigma_g^+$.[33,34] These assignments have recently come under question.[15,16,18] If the observed transitions are as assigned, however, and if the cations behave

TABLE 1: Compositions and Orbital Energies of INDO/S Molecular Orbitals from the ROHF Ground States of V_2^+, VNb^+, and Nb_2^+ [a]

	V_2^+			VNb^+			Nb_2^+		
	composition (%)			composition (%)			composition (%)		
orbital	3d	4s	energy (eV)	d	s	energy (eV)	4d	5s	energy (eV)
$d\pi_u$[b]	95	0	−13.87	95	0	−13.16	95	0	−12.65
$d\sigma_g$[c]	99	1	−12.81	90	8	−11.98	30	67	−11.63
$s\sigma_g$[c]	1	99	−11.04	8	92	−11.09	68	32	−10.91
δ_g[c]	100	0	−12.58	100	0	−12.23	100	0	−11.74
$s\sigma_u$[d]	0	96	−6.33	1	85	−6.48	1	83	−6.93
δ_u[d]	100	0	−6.16	100	0	−6.27	100	0	−6.21
$d\pi_g$[d]	67	0	−4.31	38	0	−3.84	47	0	−5.19
$d\sigma_u$[d]	100	0	−4.14	97	2	−4.58	99	0	−4.86

[a] Small contributions from p orbitals are omitted. [b] The g and u labels serve only to distinguish the bonding and antibonding combinations in the case of VNb^+. [c] Energies of open-shell ROHF orbitals do not correspond to ionization potentials, so should not be compared directly to the closed-shell orbital energies. [d] Orbital energies relative to the energy of the open-shell δ_g orbitals.

analogously, it might then be possible to observe two low-energy resonance Raman transitions in the cations.

III. Results and Discussion

A. INDO/S SCF/SOCI Calculations, Cations. *1. Self-Consistent Field Ground States.* SCF calculations on the cations displayed poor convergence behavior similar to that found for the neutrals.[15,16] As done previously, refined orbitals were obtained using the CAHF formalism.[43] The configurational space used in defining the average was obtained by fixing six electrons in the closed-shell $d\pi_u$ bonding MOs and lowest lying σ_g hybrid MO, and distributing three electrons in the remaining fifteen MOs in all possible arrangements. These calculations converged very rapidly for all three cations, and the resulting orbitals were used as the starting point for subsequent ROHF calculations. The standard ROHF calculations converged to stable ground states for V_2^+ and Nb_2^+, but additional problems were encountered with VNb^+.

In the case of VNb^+ the starting guesses for the 1σ and 2σ MOs were considerably more hybridized than they were in the homonuclear cations. A similar observation was made regarding the orbitals of VNb and was attributed to much larger s−d σ overlap.[16] This occurs because the bond distance is intermediate between those of V_2 and Nb_2 and the vanadium and niobium orbitals are of different sizes. The same phenomenon occurs in the case of VNb^+. Though in itself this is not problematic, the starting guesses for the 1σ and 2σ MOs were also very close in energy, which led to convergence problems because the two σ MOs would alternate between the closed shell and open shell during the course of SCF iterations. As a result, it proved very difficult to obtain a standard ROHF ground state for VNb^+. This problem was circumvented by adopting the nonstandard approach described above, in which an average of the occupations $1\sigma^2 2\sigma^1$ and $1\sigma^1 2\sigma^2$ was used. Oscillation of the σ orbitals between the closed shell and open shell is thus prevented by making both orbitals part of a separate open shell. An SCF calculation on VNb^+ using this model converged quickly. The resulting converged orbitals were much less hybridized and further apart in energy than the starting orbitals had been.

The ground states just described were fixed to be of $^4\Sigma^-$ symmetry with open-shell configuration $\sigma\delta^2$, in accord with the results of DFT calculations.[27] An alternative SCF ground state of $^2\Delta_g$ symmetry with configuration $\sigma^2\delta^1$ that is analogous to the $^3\Delta_g$, $\sigma^1\delta^1$ ground state of Ti_2[57−59] was investigated for V_2^+ but was found to be much higher in energy. The CI calculations described below confirm that the ground states of all three cations are of $^4\Sigma^-$ symmetry. More recent DFT calculations also found a $^4\Sigma_g^-$ ground state for V_2^+.[31]

The SCF MOs obtained for V_2^+, VNb^+, and Nb_2^+ (Table 1) are similar to those obtained for the neutral molecules.[16] As with the neutrals, the $d\sigma_g$ MO is lower in energy than the $s\sigma_g$ MO in V_2^+ and VNb^+, but higher in energy in Nb_2^+. Other differences between the neutral and cation ground states are found in the hybridizations of the σ_g orbitals of VNb^+ and Nb_2^+. In the former case, the σ MOs of VNb were considerably hybridized,[16] whereas those of VNb^+ are much less so (Table 1). In VNb the σ bonding MOs are very close in energy (separated by ~0.24 eV[16]) whereas in VNb^+ they are separated by ~0.91 eV, which could explain the different extents of hybridization in the two molecules.

In the case of diniobium, the σ_g MOs are considerably more hybridized for the cation than they are for the neutral molecule, despite the fact that the orbital energies have a similar (sizable) separation in the two cases. It is not clear why the hybridizations are different. An in-depth examination of the two electron integrals in the two cases might provide an explanation, but this was not attempted because extensive configurational mixing occurs in the CI calculations anyway.

2. Spin−Orbit Enhanced Configuration Interaction Results. The primary goal of this work is to obtain accurate estimates of the ground-state spin−orbit splittings in the cations. The magnitude of the splitting depends largely on the difference in the energies of the ground state and interacting isoconfigurational excited states. Given the highly correlated nature of their wave functions, that difference cannot be obtained accurately without a proper treatment of correlation. This is not straightforward in a semiempirical scheme like INDO/S, which incorporates some correlation directly by obtaining parameters from experiment or fitting parameters to reproduce experimental results. This implicit correlation is thought to be dynamical in nature.[38−41] Essential correlation is not incorporated in the model and must be included in cases where there are extensive essential correlation effects. This must be done without also including a partial estimation of the dynamic correlation, however, which leads to the well-known “overcounting problem” and consequent deterioration of results. This is known from fundamental considerations[3,4,14,60] and was clearly demonstrated for neutral V_2, VNb, and Nb_2.[16]

The strategy used here is the same used previously for the neutrals.[16] The general idea is to identify configurations (more properly, CSFs) making essential correlation contributions to the $X^4\Sigma^-$, $a^2\Sigma^+$, and $b^2\Sigma^-$ wave functions, and then use only those configurations in an SOCI calculation. The details are as follows: first, molecular orbitals experiencing significant localization corrections are identified through populations of antibonding MOs in ground-state CI wave functions expanded

TABLE 2: Populations of the MOs of V_2^+ Listed in Table 1 from Full CI Calculations Using the Orbitals of Each Symmetry as Active Spaces[a]

orbital	population, V_2^+	population, V_2
$d\pi_u$	3.93	3.92
$d\sigma_g$	1.88	1.94
$s\sigma_g$	0.97	1.87
$d\delta_g$	1.65	1.62
$d\delta_u$	0.35	0.39
$s\sigma_u$	0.01	0.13
$d\sigma_u$	0.12	0.07
$d\pi_g$	0.07	0.08

[a] Results for V_2[16] shown for comparison.

in active spaces restricted by symmetry (σ, π, or δ). Orbitals with important localization corrections are those with large electron populations in the antibonding combinations. The second step consists of full CI calculations using as active space the orbitals found to have large essential correlation corrections in the first step. All CSFs contributing to the $X^4\Sigma^-$ and $a^2\Sigma^+$ state wave functions with coefficients greater than 0.01 are then incorporated in the final, "essential correlation only" SOCI calculations. The value of 0.01 was chosen on the basis of careful consideration of the composition of the ground-state wave function obtained previously for V_2[16] and gave satisfactory results for the ground-state spin−orbit splittings of the neutrals. Results obtained for each step of the procedure are presented and discussed below.

Molecular orbital populations obtained for V_2^+ from CI wave functions of the $X^4\Sigma_g^-$ state expanded in active spaces of each symmetry are collected in Table 2. It should be emphasized that these results are obtained from three separate CI calculations, with active spaces restricted to the σ, π, and δ orbitals from Table 1, respectively. The dπ, dσ, and dδ MOs behave as expected on the basis of the previous results for V_2 (also found in Table 2),[16] with very limited localization of the dπ orbitals (less than 0.05 electrons in each antibonding orbital) and more significant corrections for the dσ and dδ orbitals. The occupation of the singly occupied sσ_g orbital of V_2^+, in contrast, is virtually unaffected by configuration interaction.

This result is rather surprising on naïve comparison to the neutral diatomic but simply follows the dissociative behavior of a singly occupied orbital, which does not require an essential correlation correction to the wave function. If the orbital were doubly occupied, as it is in V_2, then localized orbitals are obtained via the configurational mixing

$$^1\Psi^{H_2}_{loc} = \frac{1}{\sqrt{2}}(|\sigma_g\bar{\sigma}_g| - |\sigma_u\bar{\sigma}_u|) = \frac{1}{\sqrt{2}}(|A\bar{B}| - |\bar{A}B|) \tag{34}$$

where A and B are σ-symmetry atomic orbitals on each center and β spin electrons are indicated by the horizontal bars. The right side of eq 34 is a singlet CSF in which one atomic orbital on each center is occupied. This is directly analogous to the well-known dissociation problem of the ground-state σ_g^2 configuration of dihydrogen.[52] The singly occupied σ_g orbital in V_2^+ is then analogous to the ground state of H_2^+, which does dissociate properly without configurational mixing of the form of eq 34.[61] Because the singly occupied σ_g orbital does not then require essential correlation, the active spaces used in subsequent calculations are limited to the doubly occupied σ_g orbital, the corresponding antibonding σ_u orbital, and the four δ symmetry combinations. This gives rise to modest numbers of CSFs, 120 quartets and 210 doublets.

Tables 3−5 list all configurations contributing to the $X^4\Sigma^-$ and $a^2\Sigma^+$ states of the three cations with coefficients greater than or equal to 0.01. The essential correlation contribution to the ground-state wave function is largest for V_2^+, intermediate for VNb^+, and smallest for Nb_2^+, as shown by the respective increase in size of leading coefficient. This indicates a decrease in the multireference character of the wave function in the same order. This follows from the very compact nature of the 3d orbitals relative to the 4d orbitals, leading to a greater contribution of local character to the wave function when vanadium is present. This is known to be true in general when comparing

TABLE 3: Configurations Contributing to the $X^4\Sigma_g^-$ and $a^2\Sigma_g^+$ States of V_2^+ from Full CI in the dσ and dδ MOs Listed for V_2^+ in Table 1[a]

state	configuration	weight[b]
$X^4\Sigma_g^-$	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^2$	0.811 (0.773[c])
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_u)^2$	0.096
	$(d\pi_u)^4(d\sigma_g)^1(s\sigma_g)^1(\delta_g)^1(\delta_u)^1(d\sigma_u)^1$	0.056
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(d\sigma_u)^2$	0.034
	$(d\pi_u)^4(s\sigma_g)^1(\delta_u)^2(d\sigma_u)^2$	0.013
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(\delta_u)^2$	0.005
$a^2\Sigma_g^+$	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^2$	0.727
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_u)^2$	0.164
	$(d\pi_u)^4(d\sigma_g)^1(s\sigma_g)^1(\delta_g)^1(\delta_u)^1(d\sigma_u)^1$	0.091
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(d\sigma_u)^2$	0.035

[a] All configurations with coefficients of magnitude greater than 0.01 are listed. [b] Some of these weights are sums of contributions from more than one CSF derived from the configuation. [c] Weight of $(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^2(\delta_g)^2$ configuration in the $X^3\Sigma_g^-$ wave function of V_2, ref 16.

TABLE 4: Configurations Contributing to the $X^4\Sigma^-$ and $a^2\Sigma^+$ States of VNb^+ from Full CI in the dσ and dδ MOs Listed for VNb^+ in Table 1[a]

state	configuration[b]	weight[c]
$X^4\Sigma^-$	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^2$	0.842 (0.778[d])
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_u)^2$	0.070
	$(d\pi_u)^4(d\sigma_g)^1(s\sigma_g)^1(\delta_g)^1(\delta_u)^1(d\sigma_u)^1$	0.049
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(d\sigma_u)^2$	0.027
	$(d\pi_u)^4(s\sigma_g)^1(\delta_u)^2(d\sigma_u)^2$	0.007
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(\delta_u)^2$	0.007
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^1(\delta_u)^1$	0.002
	$(d\pi_u)^4(d\sigma_g)^1(s\sigma_g)^1(\delta_g)^2(d\sigma_u)^1$	0.001
$a^2\Sigma^+$	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^2$	0.746
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_u)^2$	0.137
	$(d\pi_u)^4(d\sigma_g)^1(s\sigma_g)^1(\delta_g)^1(\delta_u)^1(d\sigma_u)^1$	0.088
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(d\sigma_u)^2$	0.026
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^4$	0.021

[a] All Configurations with Coefficients of Magnitude Greater than 0.01 Are Listed. [b] The g and u labels serve only to distinguish the bonding and antibonding combinations. [c] Some of these weights are sums of contributions from more than one CSF derived from the configuration. [d] Weight of $(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^2(\delta_g)^2$ configuration in the $X^3\Sigma^-$ wave function of VNb, ref 16.

TABLE 5: Configurations Contributing to the $X^4\Sigma_g^-$ and $a^2\Sigma_g^+$ States of Nb_2^+ from Full CI in the sσ_g, dσ_u, and dδ MOs Listed for Nb_2^+ in Table 1[a]

state	configuration	weight[b]
$X^4\Sigma_g^-$	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^2$	0.913 (0.864[c])
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_u)^2$	0.058
	$(d\pi_u)^4(d\sigma_g)^1(s\sigma_g)^1(\delta_g)^1(\delta_u)^1(d\sigma_u)^1$	0.017
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(\delta_u)^2$	0.005
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^2(d\sigma_u)^2$	0.002
$a^2\Sigma_g^+$	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_g)^2$	0.829
	$(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^1(\delta_u)^2$	0.126
	$(d\pi_u)^4(s\sigma_g)^1(\delta_g)^4$	0.014

[a] All configurations with coefficients of magnitude greater than 0.01 are listed. [b] Some of these weights are sums of contributions from more than one CSF derived from the configuation. [c] Weight of $(d\pi_u)^4(d\sigma_g)^2(s\sigma_g)^2(\delta_g)^2$ configuration in the $X^3\Sigma_g^-$ wave function of Nb_2, ref 16.

TABLE 6: Results of INDO/S SOCI Calculations of the Energy Levels of V_2^+, VNb^+, and Nb_2^+ [a]

level of calculation	quantity	V_2^+	VNb^+	Nb_2^+
"essential correlation only" CI	Δ	18 (21[b])	77 (82[c])	145
	$E(b^2\Sigma^-)$	3000	2071	6074
	$E(a^2\Sigma^+)$	3899	4014	3180
	quartet character, $X^4\Sigma^-$ state	0.995	0.971	0.963
restricted active space full CI	Δ	57	205	244
	$E(b^2\Sigma^-)$	1215	1427	4711
	$E(a^2\Sigma^+)$	1832	2599	2961

[a] All energies are in cm^{-1} and experimental results are shown in parentheses. Δ is the spin−orbit splitting of the $X^4\Sigma^-$ ground state of each cation. [b] Reference 20. [c] Reference 18.

3d and 4d diatomics.[30,32] The same trend was observed for the leading coefficients for the neutral diatomics.[16]

Results of SOCI calculations using the configurations listed in Tables 3−5 are shown in Table 6 along with experimental results. Considering first V_2^+ and VNb^+, for which Δ has been established spectroscopically, good agreement between calculated and experimental values of the splittings are obtained. The agreement is not as close as was obtained for the neutrals, however. This is not unexpected because the INDO/S model was parametrized for neutral transition metals.[39] It is clear nonetheless that the calculations are properly accounting for the second-order spin−orbit coupling in the ground states of V_2^+ and VNb^+. The spin contamination of the ground state is larger for VNb^+, as expected because spin−orbit effects are larger for the heavier niobium atom.

The value of 145 cm^{-1} reported in Table 6 for Nb_2^+ is the first explicit estimate of the splitting of the $X^4\Sigma_g^-$ ground state of this cation. This agrees closely with the value of 142 cm^{-1} found on the basis of a difference of 3895 cm^{-1} in unperturbed energies of the $X^4\Sigma_g^-$ and $a^2\Sigma_g^+$ states obtained with DFT calculations.[27] This agreement must be considered somewhat fortuitous, however, because James et al. did not account for coupling between the isoconfigurational doublet states. This coupling is very large between the INDO/S CI wave functions for the $b^2\Sigma_g^-$ and $a^2\Sigma_g^+$ states, perturbing the energy of the lower lying $a^2\Sigma_g^+$ state to roughly 800 cm^{-1} below the unperturbed energy predicted by DFT. The inversion in the ordering of the $a^2\Sigma_g^+$ and $b^2\Sigma_g^-$ states in Nb_2^+ compared to V_2^+ and VNb^+ occurs because of the differing σ_g orbital occupations (vide infra).

The SOCI estimate of the energy of the $a^2\Sigma_g^+$ state of Nb_2^+ disagrees sharply with the energy of 13 000 cm^{-1} predicted by the CASSCF/MRCI calculations of Balasubramanian and Zhu.[35] The same calculations predicted an energy of 4984 cm^{-1} for the $b^2\Sigma_g^-$ state, in much closer agreement with the unperturbed INDO/S CI energy of 4742 cm^{-1} for this state. It is puzzling that the $a^2\Sigma_g^+$ state is estimated to be so high in energy by the CASSCF/MRCI calculations, because this state interacts with the ground state to cause the spin−orbit splitting. Second-order perturbation theory with H_{12} given by eq 8 and 13 000 cm^{-1} for $E_2^{(0)} - E_1^{(0)}$ yields only 44 cm^{-1} for Δ. This value seems too small given the trends in measured values of Δ for the neutrals (75 cm^{-1} for V_2,[17] 230 cm^{-1} for VNb,[18] 410 cm^{-1} for Nb_2[21]) and cations (V_2^+ 21 cm^{-1},[20] VNb^+ 82 cm^{-1} [18]). It should also be noted from Table 6 that the $a^2\Sigma_g^+$ state is estimated to be very low-lying for both V_2^+ and VNb^+, and the ground-state spin−orbit splittings of these cations are accurately estimated by these calculations. It therefore seems unlikely that the $a^2\Sigma_g^+$ state of Nb_2^+ has such a high energy. Unfortunately the splitting of the $X^4\Sigma_g^-$ state of Nb_2^+ has not been measured experimentally, which would allow a definitive discrimination between the varying predictions.

TABLE 7: Matrix Elements $H_{12} = \langle\Psi(X^3\Sigma^-(0^+))|\hat{H}_{S.O.}|\Psi(^1\Sigma^+(0^+))\rangle$ Determined with and without Overlap

molecule	H_{12}, no overlap (cm^{-1})	S	$\lvert C_1\rvert^2$	H_{12}, with overlap (cm^{-1})
V_2	290.0	0.0397	0.8073	283.4
VNb	593.8	0.0490	0.8532	574.6
Nb_2	897.6	0.0714	0.9183	848.3

3. Analysis of Correlation Effects in the INDO/S Model. Comparison of spin−orbit splittings computed at different levels (Table 6) allows an examination of correlation effects in the INDO/S model. The results are similar to what was found for the neutral molecules,[16] with splittings from larger active space full CI calculations much less accurate than those computed with only essential correlation contributions. This indicates that the parameters do contain some ad-hoc level of dynamic correlation. The discrepancies are in fact larger than were found for the neutrals, an unexpected result because according to the leading coefficients in the ground-state CI wave functions the cation ground states are not as highly correlated. The larger discrepancies in the case of the cations likely arise because the empirical parameters used by the method are obtained from spectroscopy of the neutral atoms, as mentioned above. If these parameters do incorporate some dynamic correlation, this correlation is appropriate for neutral atoms rather than cations. This would further complicate the "overcounting" problem. A systematically correlated semiempirical model might require a charge iterative Hamiltonian[62,63] to overcome this complication.

B. Analysis of Empirical Two State Models for Neutral Diatomics. In this section the various realizations of the empirical models developed in section II for the neutral diatomics are analyzed to determine the most effective approach. The three principal sources of error are neglect of overlap and CI in evaluating coupling matrix elements, the order at which the perturbation theory is evaluated, and the consideration of only one perturbing state. Overlap and CI are incorporated by using eq 8 for the coupling matrix element H_{12}, which requires estimates of the δ symmetry overlap integral S and the coefficients C_1 and C_2 for each molecule. These quantities are easily obtained with INDO/S CI calculations and are shown in Table 7 along with the resulting values of H_{12}. The inclusion of overlap is seen to reduce the coupling in each case, which will decrease the prediction of $E(a^1\Sigma^+)$. The trend in the other quantities in Table 7 is as expected, with the overlap increasing from V_2 to VNb to Nb_2 due to the greater extent of the 4d orbitals, and the multireference nature of the ground state decreasing as the overlap increases.

Table 8 displays values of $E(a^1\Sigma^+)$ computed at second order (eq 12), at infinite order (eq 14), and at second order with overlap for the three molecules. The INDO/S results from ref 16 are shown for comparison. All empirical predictions are seen to be too small. It is interesting to note that the least exact model, second-order perturbation theory with no overlap, gives the best results. Because inclusion of overlap and infinite order should reduce $E(a^1\Sigma^+)$ even further, limitation to two states appears to increase $E(a^1\Sigma^+)$, leading to cancellation of errors. This was found to be the case for Nb_2,[16] so it is not unreasonable to assume that the same is true for the other diatomics. It is therefore recommended for future applications to similar molecules that overlap effects be neglected and second-order perturbation theory be used.

TABLE 8: Predictions for $E(a^1\Sigma^+)$ Made with Several Empirical Two-State Models[a]

model	$E(a^1\Sigma^+)$ given by	V_2 ($\Delta = 75$ cm^{-1})	VNb (230 cm^{-1})	Nb_2 (410 cm^{-1})
second order, no overlap	$(H_{12}^2 + 2\Delta^2)/\Delta$	1271	1993	2785
second order with overlap	$((H'_{12})^2 + 2\Delta^2)/\Delta$	1221	1896	2575
infinite order, no overlap	$(H_{12}^2 + \Delta^2)/\Delta$	1196	1763	2375
INDO/S		1306 (Δ 75 cm^{-1})	2014 (232 cm^{-1})	2705 (419 cm^{-1})

[a] H_{12} is the coupling matrix element without overlap, and H'_{12} is the matrix element with overlap, eq 8.

TABLE 9: Results of Empirical Three-State Model (Details in Text) for Energy Levels of V_2^+ and Nb_2^+[a]

molecule	$E(b^2\Sigma^-)$	$E(a^2\Sigma^+)$	quartet character, $X^4\Sigma^-(^1/_2)$ level
V_2^+ ($\Delta = 21$ cm^{-1})[b]	2476	3298	0.993
V_2^+ ($\Delta = 18$ cm^{-1})[c]	3006 (3000[c])	3826 (3898[c])	0.995 (0.995[c])
Nb_2^+ ($\Delta = 145$ cm^{-1})[c]	5480 (6074[c])	4009 (3180[c])	0.964 (0.963[c])

[a] All energies are in cm^{-1} and INDO/S SOCI results from Table 6 are shown in parentheses. Δ is the spin−orbit splitting of the $X^4\Sigma^-$ ground state of each cation. [b] Experiment, ref 20. [c] Calculated (Table 6).

C. Empirical Three State Model for Cations. In this section the three-state empirical model developed earlier is applied to V_2^+ and Nb_2^+. In applying eqs 25 and 26 for $E(a^2\Sigma_g^+)$ and $E(b^2\Sigma_g^-)$, the experimental value of 21 cm^{-1} is used for Δ for V_2^+ [20] and the calculated value of 145 cm^{-1} (Table 6) is used for Nb_2^+. H_{12} is computed with eq 8 using $\bar{\zeta}_{(n-1)d}$ as defined previously. Because the open-shell σ orbital is of sσ character in V_2^+ and dσ character in Nb_2^+, eq 29 is used for ΔE in the former case, and eq 30 in the latter. The resulting values are −697 cm^{-1} for V_2^+ and 1120 cm^{-1} for Nb_2^+. It should be noted here that this inversion in sign agrees with the order of state energies found for the two molecules with SOCI calculations (Table 6).

Table 9 displays state energies and quartet character computed according to eqs 25, 26, and 31 for V_2^+ and Nb_2^+. Though the basic features of the isoconfigurational interactions proposed to cause the ground-state splittings in the cations are demonstrated by these results, agreement with the SOCI results of Table 6 is much poorer than was found with the neutral molecules (Table 8). The energies and wave functions are very sensitive to both Δ and ΔE, however. If the SOCI value of 18 cm^{-1} for Δ of V_2^+ is used instead of the experimental value of 21 cm^{-1}, for example, very close agreement is achieved between the empirical and SOCI results (second row of Table 9). The energies computed empirically for the $a^2\Sigma^+$ and $b^2\Sigma^-$ states of V_2^+ using $\Delta = 21$ cm^{-1} are likely better estimates than the SOCI energies because of the discrepancy in Δ.

The empirical-state energies computed for Nb_2^+ have large errors when compared to the SOCI predictions. In this case it is likely that the empirical estimate of $\Delta E = +1120$ cm^{-1} is too large. When spin−orbit coupling is not included in the INDO/S calculations, an unperturbed energy of 4441 cm^{-1} is obtained for $a^2\Sigma^+$. When spin−orbit interaction with $b^2\Sigma^-$ is included, the $a^2\Sigma^+$ state moves to much lower energy (3180 cm^{-1}, Table 6), indicating that the interaction is very large and hence that the states are quite close in energy. In fact, ΔE from CI calculations without the spin−orbit interaction is only on the order of +300 cm^{-1}. Unfortunately, the second-order wave functions for the $a^2\Sigma^+$ and $b^2\Sigma^-$ states of eqs 32 and 33 are badly divergent with this value of ΔE, but clearly reducing the difference in energies of these coupled states from 1120 to 300 cm^{-1} will lead to a much larger difference in their energies predicted by the empirical model, more in accord with the SOCI results. Matrix diagonalization should be used in cases where the difference in state energies is smaller than the coupling matrix element, but it is unclear how to develop such a model for three states.

4. Conclusions

A. INDO/S SOCI Calculations on V_2^+, VNb^+, and Nb_2^+. INDO/S SOCI calculations yielded $X^4\Sigma^-$ ground states for V_2^+, VNb^+, and Nb_2^+ in accord with previous experimental and theoretical studies.[18,20,27,31,35] Ground-state spin−orbit splittings in good agreement with experiment were obtained for V_2^+ and VNb^+. The prediction of 145 cm^{-1} for the splitting in Nb_2^+ (the first estimate made with a method that explicitly accounts for spin−orbit coupling) agreed well with a prediction of 142 cm^{-1} made on the basis of DFT state energies.[27] In all three cases both isoconfigurational $a^2\Sigma^+$ and $b^2\Sigma^-$ states were contaminated with quartet spin character, even though only the $a^2\Sigma^+$ state interacts directly with the ground state. This occurs due to second-order spin−orbit coupling between doublet states.

The ground-state spin−orbit splitting depends strongly on the relative energies of the three isoconfigurational states, and those energies in turn depend strongly on obtaining a reasonable approximation of the correlation energy for each state. The INDO/S SOCI calculations were designed to isolate essential correlation in the three states to avoid the well-known problem of "overcounting" the dynamical correlation incorporated into the semiempirical parameters.[3,60] Much better results were obtained using this method compared to larger restricted active space full CI calculations that also incorporated some dynamical correlation. The discrepancies in results were larger for the cations than for the neutrals, suggesting that semiempirical parameters fixed for neutral atoms contain an averaged dynamic correlation contribution that is most appropriate for neutral species. This complicates the overcounting problem when the method is used with charged species. Semiempirical methods that use charge-dependent parameters[62,63] might therefore be a better choice for charged transition metal clusters and complexes.

B. Empirical Models for Predicting Interacting State Energies. An analysis of approximations involved in empirical models[18,22] for predicting perturbing-state energies given measured values of spin−orbit splittings was carried out. It was found that second-order perturbation theory with neglect of overlap and CI in matrix elements gives the best results. This arises due to cancellation of the errors incurred by these approximations with the error incurred by limiting the number of states. An empirical model treating interactions between the $X^4\Sigma^-$, $a^2\Sigma^+$, and $b^2\Sigma^-$ states of the cations was developed along these lines, using integrals obtained from atomic energy levels[55] to fix the (unperturbed) energy difference between the excited doublet states. This model gave excellent agreement with the SOCI results for V_2^+ if the SOCI value of the ground-state splitting (18 cm^{-1} versus experiment 21 cm^{-1} [20]) is used in the model.

The same model did not give good results for Nb_2^+. In this case, however, the difference in the energies of the excited doublet states was obtained from much less reliable Racah parameters for niobium. The resulting value of ΔE did not agree with the unperturbed energy difference found with INDO/S CI calculations. ΔE obtained from the CI calculation was small enough that the second-order wave functions used in the empirical model were divergent. Caution is indicated in using empirical models at this level for cases that have pronounced near-degeneracy effects.

Acknowledgment. Funding for the calculations carried out at the Quantum Theory Project was provided by the National Science Foundation, the Office of Naval Research, and the IBM corporation. Calculations performed at Indiana University were funded by National Science Foundation grant CHE-9982415. Professor Philip Brucat at the University of Florida and Professor Ernest Davidson and Dr. Feiwu Chen at Indiana University are acknowledged for meaningful discussion of this work. Professor Davidson is acknowledged for his critical reading of the manuscript prior to submission.

References and Notes

(1) Castleman, A. W., Jr.; Bowen, K. H., Jr. *J. Phys. Chem.* **1996**, *100*, 12911−12944.

(2) Estiú, G. L.; Cory, M. G.; Zerner, M. C. *J. Phys. Chem. A* **2000**, *104*, 233−242.

(3) Martin, C. H. *Chem. Phys. Lett.* **1996**, *257*, 229−237.

(4) Freed, K. F. In *Structure and Dynamcs of Atoms and Molecules: Conceptual Trends*; Calais, J. L., Kryachko, E. S., Eds.; Dordrecht: The Netherlands, 1995.

(5) Martin, C. H.; Freed, K. F. *J. Chem. Phys.* **1994**, *101*, 4011−4027.

(6) Martin, C. H.; Freed, K. F. *J. Chem. Phys.* **1996**, *105*, 1437−1450.

(7) Martin, C. H.; Freed, K. F. *J. Phys. Chem.* **1995**, *99*, 2701−2716.

(8) Martin, C. H.; Freed, K. F. *J. Chem. Phys.* **1994**, *101*, 5929−5941.

(9) Martin, C. H.; Freed, K. F. *J. Chem. Phys.* **1994**, *100*, 7454−7470.

(10) Kanzler, A. W.; Freed, K. F.; Sheppard, M. G. *Int. J. Quantum Chem.* **1992**, *44*, 643−674.

(11) Kanzler, A. W.; Freed, K. F.; Sun, H. S. *J. Chem. Phys.* **1992**, *96*, 5245−5252.

(12) Kanzler, A. W.; Freed, K. F. *J. Chem. Phys.* **1991**, *94*, 3778−3789.

(13) Wang, X. C.; Freed, K. F. *J. Chem. Phys.* **1989**, *91*, 1151−1166.

(14) Löwdin, P. O. *Int. J. Quantum Chem.* **1999**, *72*, 379−391.

(15) O'Brien, T. A.; Albert, K.; Zerner, M. C. *J. Chem. Phys.* **2000**, *112*, 3192−3200.

(16) O'Brien, T. A.; Albert, K.; Zerner, M. C. *J. Chem. Phys.* **2000**, *113*, 2203−2213.

(17) Langridge-Smith, P. R. R.; Morse, M. D.; Hansen, G. P.; Smalley, R. E.; Merer, A. J. *J. Chem. Phys.* **1984**, *80*, 593−600.

(18) James, A. M.; Kowalczyk, P.; Langlois, E.; Campbell, M. D.; Ogawa, A.; Simard, B. *J. Chem. Phys.* **1994**, *101*, 4485−4495.

(19) James, A. M.; Kowalczyk, P.; Fournier, R.; Simard, B. *J. Chem. Phys.* **1993**, *99*, 8504−8517.

(20) Yang, D. S.; James, A. M.; Rayner, D. M.; Hackett, P. A. *J. Chem. Phys.* **1995**, *102*, 3129−3134.

(21) Van Zee, R. J.; Li, S.; Weltner, W. *Chem. Phys. Lett.* **1994**, *217*, 381−386.

(22) Spain, E. M.; Behm, J. M.; Morse, M. D. *J. Chem. Phys.* **1992**, *96*, 2511−2516.

(23) James, A. M.; Kowalczyk, P.; Simard, B. *Chem. Phys. Lett.* **1993**, *216*, 512−518.

(24) James, A. M.; Kowalczyk, P.; Simard, B. *J. Mol. Spectrosc.* **1994**, *164*, 260−274.

(25) Grönbeck, H.; Rosén, A. *J. Chem. Phys.* **1997**, *107*, 10620−10625.

(26) Weber, S. E.; Rao, B. K.; Jena, P.; Stepanyuk, V. S.; Hergert, W.; Wildberger, K.; Zeller, R.; Dederichs, P. H. *J. Phys.-Condens. Mater.* **1997**, *9*, 10739−10748.

(27) Simard, B.; James, A. M.; Kowalczyk, P.; Fournier, R.; Hackett, P. A. *Proc. SPIE* **1994**, *2124*, 376.

(28) Salahub, D. R.; Baykara, N. A. *Surf. Sci.* **1985**, *156*, 605.

(29) Walch, S. P.; Bauschlicher, C. W.; Roos, B. O.; Nelin, C. J. *Chem. Phys. Lett.* **1983**, *103*, 175−179.

(30) Walch, S. P.; Bauschlicher, C. W., Jr. Thoeretical Studies of Transition Metal Dimers. In *Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules*; Bartlett, R. J., Ed.; Reidel: Dordecht, The Netherlands, 1985; pp 17−51.

(31) Gutsev, G. L.; Bauschlcher, C. W. *J. Phys. Chem. A* **2003**, *107*, 4755−4767.

(32) Siegbahn, P. E. M. Electronic structure calculations for molecules containing transition metals. In *Advances in Chemical Physics*; Prigogine, I., Rice, S. A., Eds.; John Wiley & Sons: New York, 1996; Vol. 93.

(33) Cossé, C.; Fouassier, M.; Mejean, T.; Tranquille, M.; DiLella, D. P.; Moskovits, M. *J. Chem. Phys.* **1980**, *73*, 6076−6085.

(34) Hu, Z.; Shen, B.; Zhou, S.; Deosaran, S.; Lombardi, J. R.; Lindsay, D. M. *SPIE* **1991**, 1599.

(35) Balasubramanian, K.; Zhu, X. L. *J. Chem. Phys.* **2001**, *114*, 10375−10388.

(36) DaBell, R. S.; Meyer, R. G.; Morse, M. D. *J. Chem. Phys.* **2001**, *114*, 2938−2954.

(37) Yang, D.-S.; Simard, B.; Hackett, P. A.; Bréces, A.; Zgierski, M. Z. *Int. J. Mass Spectrom. Ion Processes* **1996**, *159*, 65−74.

(38) Zerner, M. C. Semiempirical Molecular Orbital Methods. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: 1991; Vol. 2, pp 313−363.

(39) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589−599.

(40) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21−54.

(41) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111−134.

(42) Zerner, M. C.; Ridley, J. E.; Bacon, A. D.; Edwards, W. D.; Head, J. D.; McKelvey, J.; Culberson, J. C.; Knappe, P.; Cory, M. G.; Weiner, B.; Baker, J. D.; Parkinson, W. A.; Kannis, D.; Yu, J.; Rösch, N.; Kotzian, M.; Tamm, T.; Karelson, M. M.; Zheng, X.; Pearl, G. M.; Broo, A.; Albert, K.; Cullen, J. M.; Cramer, C. J.; Truhlar, D. G.; Li, J.; Hawkins, G. D.; Liotard, D. A. *ZINDO−A semiempirical program package*; University of Florida: Gainesville, FL.

(43) Zerner, M. C. *Int. J. Quantum Chem.* **1989**, *35*, 567−575.

(44) Edwards, W. D.; Zerner, M. C. *Theor. Chim. Acta* **1987**, *72*, 347−361.

(45) Pauncz, R.; McKelvey, J.; Zerner, M. C. Unpublished.

(46) Pauncz, R. *Spin Eigenfunctions: Construction and Use*; Plenum Press: New York, 1979.

(47) Kotzian, M.; Rösch, N.; Pitzer, R. M.; Zerner, M. C. *Chem. Phys. Lett.* **1989**, *160*, 168−174.

(48) Manne, R.; Zerner, M. C. *Int. J. Quantum Chem. Symp.* **1986**, *19*, 165.

(49) Kotzian, M.; Rösch, N.; Zerner, M. C. *Int. J. Quantum Chem. Symp.* **1991**, *25*, 545−555.

(50) Lefebvre-Brion, L.; Field, R. W. *Perturbations in the Spectra of Diatomic Molecules*; Academic: Orlando, 1986.

(51) This assumes equal weighting of the vanadium and niobium orbitals in the σ and δ bonding MOs, as assumed by James et al.[18] in determining spin−orbit matrix elements.

(52) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; McGraw-Hill: New York, 1989.

(53) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

(54) Slater, J. C. *Quantum Theory of of Atomic Structure*; McGraw-Hill: New York, 1960; Vol. 1.

(55) Anno, T.; Teruya, H. *J. Chem. Phys.* **1970**, *52*, 2840−2848.

(56) Bersuker, I. B. *Electronic Structure and Properties of Transition Metal Compounds*; John Wiley and Sons: New York, 1996.

(57) Doverstål, M.; Lindgren, B.; Sassenberg, U.; Morse, M. D. *J. Chem. Phys.* **1992**, *97*, 7087−7092.

(58) Doverstål, M.; Karlsson, L.; Lindgren, B.; Sassenberg, B. *Chem. Phys. Lett.* **1997**, *270*, 273−277.

(59) Bauschlicher, C. W., Jr.; Partridge, H.; Langoff, S. R.; Rosi, M. *J. Chem. Phys.* **1991**, *95*, 1057.

(60) Martin, C. H.; Birge, R. R. *J. Phys. Chem. A* **1998**, *102*, 852−860.

(61) More rigorously, in this specific case of a single electron the configurations $|\sigma_g\rangle = A + B$ and $|\sigma_u\rangle = A - B$ are degenerate in the limit of zero interaction and could thus be added or subtracted to yield the wave function $|A\rangle$ or $|B\rangle$, respectively. Quantum mechanics is unable to distinguish between these two cases, however, and can give only the probability of 50% that one or the other will occur when the bond is broken. Thus both $|\sigma_g\rangle$ and $|\sigma_u\rangle$ are valid wave functions, and completely equivalent at infinite separation. The important point for the present discussion is that an essential correlation correction to $\Psi = |\sigma_g\rangle$ is not necessary as the bond length increases.

(62) Baker, J. D.; Zerner, M. C. *J. Phys. Chem.* **1990**, *94*, 2866−2872.

(63) Baker, J. D.; Zerner, M. C. *J. Phys. Chem.* **1991**, *95*, 2307−2311.