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Multireference Correlation Calculations for the Ground States of $VO^{+/0/-}$ Using Correlation Consistent Basis Sets

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Highly correlated multireference calculations for the ground states of the $VO^{+/0/-}$ species are presented. We use extrapolation techniques to estimate correlation energies at the basis set limit. Correlation consistent basis sets for vanadium have been constructed for this purpose. Binding energies, bond distances, and vibrational frequencies have been calculated. Excellent agreement between the calculated and experimental values is reached for the cation and the neutral molecule. We present highly accurate theoretical estimates for the properties of the VO anion. Furthermore, we confirm previous assignments of its ground state which is found to be $^3\Sigma^-$.

1. Introduction

Vanadium oxide species have been subject to many current experimental and theoretical studies[1−28] where the electronic structure of the ground states, as well as equilibrium geometries, vibrational frequencies, and chemical reactivity were examined. The simplest molecule, VO, and corresponding singly charged species seem to be well characterized.[15,16,24,29] However, most of the published theoretical studies for $VO^{+/0/-}$ present results of different density functional calculations using a variety of different basis sets and exchange-correlation functionals. Because density functional calculations are based on a single-reference formalism, it is not obvious if they are suitable to describe the ground-state properties of VO species correctly. For instance, the MR-CISD (multireference configuration interaction with single and double excitations) study of Nakao et al.[24] clearly indicates a multiconfigurational nature of the ground state of the VO^+ cation: the weight of the leading configuration is 0.89.

In this work, we present results of multireference correlation calculations for all three VO species, cation, neutral molecule, and anion. We use an extrapolation technique to estimate the electronic correlation energy at the basis set limit. For this purpose, we have constructed correlation consistent basis sets for the vanadium atom. The details of the calculations will be presented in the section 2 followed by sections 3 and 4 which contain results and discussion.

Finally, we discuss the question of the assignment of the ground state of the VO anion, for which no consensus between experimental[7] and theoretical[15,16] studies exists so far.

2. Details of the Calculation

2.1. Methods. In the classical picture, a chemical bond between a transition metal atom and an oxygen atom arises from the interaction of the $3d_\sigma$ and $3d_\pi$ orbitals of the metal atom with the corresponding σ- and π-like counterparts of the 2p shell of the oxygen atom. The 4s orbital might also be involved in the bonding, especially in the anionic species. $3d_\delta$ orbitals cannot interact with any oxygen orbitals and are classified as nonbonding.

Thus, for an accurate description of bonding in VO, at least the 3d(V), 4s(V), and 2p(O) atomic orbitals have to be explicitly considered. We use the complete active space self-consistent field (CASSCF) method to construct corresponding molecular orbitals. In the first step, we perform a state-averaged CASSCF calculation over the seven lowest states of VO^+. The active space consists of the 8σ, 1π, 9σ, 2π, 10σ, and 11σ molecular orbitals and contains 8 electrons.

The resulting orbitals are a good start for the second orbital optimization step which comprises a CASSCF calculation for the particular ground state of the particular VO species. The active space is the same as given above and contains 8, 9, or 10 electrons for cation, neutral molecule, and anion, respectively. This two-step procedure greatly facilitates convergence to the CASSCF wave function in which the active orbitals are as intended.

Dynamical electron correlation is included through the multireference average coupled-pair-functional (MR-ACPF) method,[30] which is a size-consistent variant of the MR-CI approach. As the multiconfigurational reference, we use the CASSCF wave function from the second orbital optimization step. Additionally to the active electrons of the CASSCF calculation, the 2s(O) electrons are also correlated. Only single and double excitations to the external orbitals are taken into account in the MR-ACPF calculations. Occasionally, electrons in the so-called semi-core 3s(V)- and 3p(V)-like orbitals are also correlated (this will be mentioned explicitly when corresponding results will be discussed).

To estimate the electronic correlation energy at the basis set limit Truhlar's two-point-extrapolation[31] is applied

$$E_{\mathrm{corr}}^{\mathrm{BSL}} = \frac{E_{\mathrm{corr}}^{\mathrm{X1}} X_1^3 - E_{\mathrm{corr}}^{\mathrm{X2}} X_2^3}{X_1^3 - X_2^3}$$

where X_1 and X_2 are the so-called cardinal numbers which characterize the size of two subsequent basis sets, i.e., $X = 2$, 3, ..., etc. for basis sets of double-ζ (DZ), triple-ζ (TZ), ..., etc.

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TABLE 1: Composition of the Correlation Consistent Basis Sets for the Vanadium Atom

basis set	un-contracted functions	contracted functions	polarization functions
DZ	(14s 8p 4d) + p	⟨ 6s 4p 2d ⟩	(2f) → ⟨ 1f ⟩
TZ	(17s 10p 5d) + p	⟨ 8s 5p 3d ⟩	2f 1g
QZ	(20s 12p 6d) + p	⟨ 10s 6p 4d ⟩	3f 2g 1h
5Z	(23s 14p 7d) + p	⟨ 12s 7p 5d ⟩	4f 3g 2h 1i

quality; $E_{\mathrm{corr}}^{\mathrm{X1}}$ and $E_{\mathrm{corr}}^{\mathrm{X2}}$ are the values of the correlation energies calculated using the basis X_1 and X_2, respectively. $E_{\mathrm{corr}}^{\mathrm{BSL}}$ is the estimation of the correlation energy value at the basis set limit (BSL). Throughout this work, we use basis sets of QZ ($X = 4$) and 5Z ($X = 5$) quality to predict $E_{\mathrm{corr}}^{\mathrm{BSL}}$.

All ab initio calculations have been performed using the MOLPRO package versions 2000.1/2002.1.[32] (For the details about the calculation of vibrational frequencies, see subsection 2.3.)

We also present results of spin-unrestricted density-functional calculations using the B3LYP[33−36] and BP86[34,37] exchange-correlation functionals. These calculations have been performed by the TURBOMOLE program[38,39] with cc-pVTZ basis sets for both atoms and all three VO species.

2.2. Basis Sets. It has been shown[40] that extrapolation techniques work well only if the basis sets used in the individual calculations fulfill certain requirements, i.e., the so called correlation consistency which was extensively analyzed by Dunning and co-workers.[41] They also have developed series of the correlation consistent basis sets for the main group atoms up to the fourth period.[42] Unfortunately, no such basis sets exist for transition metal atoms (apart from a few exceptions). (Noro et al.[43] have developed a series of correlation consistent basis sets for vanadium which describe, however, mainly the correlation of the 4s and 4p shells.) For this reason, we have constructed a series of correlation consistent basis sets for the vanadium atom of DZ through 5Z quality. The composition of the constructed basis sets is shown in Table 1.

The uncontracted basis functions representing the strongly occupied atomic orbitals (s, p, and d orbitals) are optimized at the density functional level using a new basis set optimizer.[44] Flat exponents for the valence shell obtained from the optimizer have sometimes "gaps" between different atomic shells (especially s exponents). Therefore, and from the reason which will become clear below they are replaced by even-tempered sequences.

Thereafter split-valence general contraction scheme which goes back to Raffenetti[45] is used to combine obtained basis functions to (1) sets of fully contracted single functions for the 1s, 2s, and 2p core orbitals and (2) sets containing X functions (contracted and uncontracted, X is the cardinal number of the corresponding basis set) for the subvalence 3s and 3p as well as valence 3d and 4s orbitals. Contraction coefficients are taken from the state-averaged CASSCF calculations for the ground states of V^0 ($3d^3$ $4s^2$, ^4F) and V^{+1} ($3d$,^{4} ^5D).

Polarization functions are optimized for the contracted basis sets as obtained from the basis set optimizer. A three-step procedure based on atomic CISD calculations is used. In the first CISD-step, exponents of all polarization functions for the 3d shell, i.e., f and higher (up to $l_{\max} = X + 1$, where X is the cardinal number of a given basis), are optimized as even-tempered sets by calculations for the ground state of V^{+2} ($3d^3$, ^4F). The number of polarization functions of each kind is given by $n = X - l + 1$ (except for the DZ basis, for which two contracted f functions are used).

In the second CISD step, a set of polarization functions for the 4s shell (p and higher, up to $l_{\max} = X - 1$) has its turn. In contrary to the upper scheme, in which the number of polarization functions was dependent on the size of the basis set (X) and the kind of the function (l), we tempt to use only one function of each kind to polarize the 4s shell. For this purpose, it is necessary to add a diffuse p function because the p function with the smallest exponent obtained from the basis set optimizer is too tight for being suitable to polarize the 4s shell. However, we have found that no additional functions with $1 < l \leq X - 1$ are needed for the polarization of the 4s shell: it is sufficient to let the available functions with the smallest exponent to become even more diffuse. To optimize the exponents of the functions with $1 \leq l \leq X - 1$ CISD calculations for the ground state of V^0 ($3d^3$ $4s^2$, ^4F) are used.

In the third CISD step, polarization functions with $l \leq X - 1$ are "redistributed" equally in the space between the largest exponent values obtained in the first CISD step and the smallest values from the second CISD step. Thereafter, these sets of polarization function are suitable to polarize both 3d and 4s shells. Functions with $X - 1 < l < l_{\max}$ are left unchanged from the first CISD step. (Correlation consistent basis sets for vanadium described here are available via Supported Information section and on demand.)

For oxygen, we use cc-pVXZ basis sets of Dunning[46] in the case of cation and neutral molecule, aug-cc-pVXZ basis sets[47] for the anion. (In the calculations for the anion, we do not use augmented basis sets for vanadium which have not been constructed yet. Oxygen has a much higher electronegativity so that the probability of finding the extra electron will be much higher at an oxygen site than at a vanadium site.)

For geometry optimizations and calculations of the potential energy curves, we use basis sets of the TZ quality.

2.3. Calculation of the Vibrational Frequencies. To calculate anharmonic vibrational frequencies for all of the VO species, we use the LEVEL (version 7.4) program,[48] which solves the radial Schrödinger equation. The potential energy curves for the ground states of all species are calculated in the range of V−O bond distances (R_{VO}) between 1.2 and 3.0 Å. For $R_{\mathrm{VO}} < 1.2$ Å, the potential curves are approximated using cubic spline three-point-interpolation over $R^2 \times \mathrm{V}(R)$ values. For $R_{\mathrm{VO}} > 3.0$ Å, values of $R \exp(-bR)$ are used.

The absolute energetic position of the first vibrational levels with respect to the asymptote is also calculated by the LEVEL program. We use the $\nu = 0$ energies to evaluate the D_0 dissociation energies. The anharmonic vibrational frequencies (ν_1) given in the Table 5 are obtained as the difference between the $\nu = 1$ and 0 energy levels.

The corresponding harmonic frequencies (ω_e) are obtained from the second derivatives of the potential energy curves at the equilibrium distance of the respective VO species.

3. Quality Checks for the Vanadium Basis Sets

3.1. Ionization Potentials for Vanadium. To check whether the constructed basis sets for vanadium are suitable for the extrapolation of the correlation energy, i.e., the basis sets fulfill the requirements of the correlation consistency, we have calculated the first three ionization potentials of vanadium. The results of the MR-ACPF calculations are collected in the Table 2.

We find relatively large difference between the calculated XZ value and experimental value for the first ionization potential IP_1. This error is caused by relativistic effects which have not been considered so far. If we calculate expectation values of the mass−velocity and Darwin terms (at the Hartree−Fock level

TABLE 2: Calculated and Experimental Values (eV) of the First Tree Ionization Potentials of the Vanadium Atom

basis set	IP_1	IP_2	IP_3	%[a] of E_{corr}
DZ	6.40	14.17	28.82	70
TZ	6.34	14.20	28.83	90
QZ	6.38	14.21	28.84	96
5Z	6.39	14.23	28.85	98
XZ[b]	6.40	14.25	28.86	100[c]
+rc[d]	6.67	14.14	28.67	
exp.	6.74	14.65	29.31	

[a] Mean percentage of the covered correlation energy. [b] Extrapolated value using Truhlar's formula and QZ/5Z basis sets. [c] Expected BSL-value. [d] Relativistic corrections added to the XZ values.

using 5Z basis set) for neutral V atom and V^{+1}, we find that the energy difference between their ground states is increased by 0.27 eV. (Our result is similar to that of Osanai et al.[49] They have found 0.29 eV.)

This large effect is caused by the 4s orbital which is doubly occupied in the ground state of the neutral vanadium atom ($3d^34s^2$) and not occupied after the ionization ($3d^4$). Adding this correction to the nonrelativistic value of IP_1 yields 6.67 eV and the deviation from the experimental value becomes only 0.07 eV. The relativistic correction have also been added to the IP_2 and IP_3 values.

Compared to the measured (spin−orbit averaged) data, our calculated IPs are systematically too small, probably due to the lack of correlation of semicore 3s and 3p electrons. Anyhow, we find a quite satisfactory agreement between the theory and experiment.

Besides the results for the ionization potentials, we also give the average percentage of the correlation energy recovered by different basis sets. This fraction increases continuously from 70% for the DZ basis to 98% for the 5Z basis. The difference between the two subsequent basis sets is systematically getting smaller the larger the basis sets becomes. This well-known slow convergence actually necessitates the extrapolation step.

It is obvious that the basis sets we have constructed are suitable to describe any of the first four oxidation states of vanadium atom with a high accuracy. Furthermore, the series of the constructed basis sets exhibits typical convergence feature which is expected from correlation consistency principles. Thus, the application of our basis sets to the ground states of vanadium oxide species (which are main target systems of our studies) is well justified.

3.2. Ground-State Properties of VO^+. There are numerous theoretical studies on the ground-state electronic structure of the VO^+ cation and its spectroscopic constants.[20,24,28,29,50,51] Therefore, VO^+ is a good test case to assess the quality of our new vanadium basis sets. Table 3 shows results of our calculations together with computational and experimental data from the literature.

The bond lengths obtained in various density functional studies are remarkably similar and show good agreement with the experimental value. Ab initio calculations including electron correlation, especially multireference methods, tend to slightly overestimate the bond distance. These deviations are, however, small (a few hundredth of Å). The reason for this small error is lack of the correlation of semicore 3s(V) and 3p(V) electrons. Taking them into account leads to $R_e = 1.559$ Å.

Calculation of the dissociation energy is a more difficult task: B3LYP results underestimate it by almost 0.5 eV (except the result of Shiota and Yoshizawa[51] which agrees quite well with the experimental values), whereas pure density functional methods overestimate it by almost the same amount. More accurate results are obtained by high-level correlation methods, although these results depend strongly on chosen basis set (as seen from the discrepancy between our MR-ACPF result and that of Schröder et al.[28]).

TABLE 3: Calculated Ground State Properties of VO^+

method	R_e, Å	D_e, eV	D_0, eV	ω_e, cm^{-1}	ν_1, cm^{-1}	ref
Density Functional Calculations						
B3LYP	1.538	5.59	5.52	1148	1136	this work
HF-Slater	1.536			1150		52
B3LYP	1.532	5.95		1160		51
B3LYP	1.533			1184		20
B3LYP	1.539		5.56			24
B3LYP	1.54	5.68				28
BP86	1.548	6.58	6.51	1117	1107	this work
DFT	1.54		6.89	1146		50
BLYP	1.559		6.36			24
BOP	1.558		6.42			24
Wave Function Based Methods						
MR-ACPF	1.563	5.98	5.91	1084	1058	this work
HF	1.501			1380		52
GVBCI-SCF	1.56	5.56		1108		53
CASSCF	1.546		5.60			24
MR−CISD	1.566		5.85			24
MR-CISD+Q	1.571		5.83			24
CCSD(T)	1.54	5.75				28
MR-ACPF	1.57	5.25				28
exp.	1.54	5.99		1060		29

Computational results obtained for vibrational frequencies mainly come from single-reference calculations. Although it is no surprise that the harmonic frequency is much too high at Hartree−Fock level, we note that density functional methods also overestimate this property by almost 100 cm^{-1}. Better agreement between the experimental and theoretical values is reached if one goes beyond the single-reference formalism (GVBCI or MR-ACPF). This is caused by the multireference character of the ground state. Even at the equilibrium distance the weight of the leading configuration $|...8\sigma^2 3\pi^4 1\delta^2|$ in the CASSCF wave function is only 88% and becomes smaller while molecule dissociate. This leads to a increasingly poor description of the potential energy curves by single-reference methods at distances which deviate more and more from the equilibrium bond distance.

3.3. Ground-State Properties of VO. Like the cation, the neutral VO molecule has been extensively studied theoretically in the past.[2,3,6,13−16,20,26,52,54−58] We use it as a test system to demonstrate the strength of our approach which will be applied to calculate properties of the VO^- anion. The latter system was much less studied and will be discussed in detail in section 4. Calculated spectroscopic constants of the neutral VO molecule are collected in the Table 4.

Similar to the cation, all methods perform quite good for the bond distance. Deviations of a few hundredth of Å from the experimental value are typical for calculations with medium basis sets. Again, our MR-ACPF calculation slightly overestimates the equilibrium distance. Our value reduces from 1.593 to 1.589 Å after including the correlation of the 3s(V) and 3p(V) electrons.

Binding energies calculated by density functional methods also follow similar trends as we have already seen for the cation: apart from a few exceptions, B3LYP slightly underestimate dissociation energies, whereas pure DFT methods overestimate them by about 1 eV compared to the experimental value. The dissociation energies reported by Vyboishchikov and Sauer[16] differ by more than 1 eV from other density functional results reported in the literature. The discrepancy probably stems

TABLE 4: Calculated Ground State Properties of VO

method	R_e, Å	D_e, eV	D_0, eV	ω_e, cm^{-1}	ν_1, cm^{-1}	ref
Density Functional Calculations						
B3LYP	1.579	6.22	6.15	1065	1057	this work
HF−Slater	1.567			1068		52
B3LYP	1.580		6.54	1044		15
B3LYP	1.590	5.28				16
B3LYP	1.569		6.27	1116		20
B3LYP	1.58				1018	58
B3LYP	1.589		6.42	1037		26
BP86	1.585	7.46	7.41	1043	1034	this work
BP86	1.60		7.50	1028		57
BPW91	1.586		7.81	1018		15
BLYP	1.598		7.44	1002		15
BP86	1.596	6.32				16
Wave Function Based Methods						
MR-ACPF	1.593	6.44	6.38	1035	1022	this work
HF	1.534			1288		52
CISD	1.565			1083		54
CPF	1.604		5.68	959		54
UCCSD(T)	1.602		6.32	1028		56
MR-ACPF	1.554		5.43			6
MCPF	1.588	6.06		1003		14
AIMP-MCPF	1.586	6.09		1008		14
exp.	1.589	6.48 (± 0.09)[a]		1011		29

[a] See G. Balducci et al.[59]

from the treatment of the atomic asymptotes. The ab initio calculations show quite large variations. Although our MR-ACPF result shows the closest agreement with experimental data, we point out that the UCCSD(T) results of Bauschlicher and Langhoff[54] are also quite close.

Most of the calculated vibrational frequencies are close to the measured value. Except the B3LYP value of Calatayud et al.,[20] there are only small variations among results of density functional studies. B3LYP overestimates the vibrational frequency by about 10−50 cm^{-1}, and pure density functional methods perform slightly better. One should also keep in mind that harmonic frequencies are about 10 cm^{-1} larger than anharmonic values which are observed in experiments. Furthermore, the multireference character of the ground state should also be taking into account. (Similar to the situation of the cation, the weight of the leading configuration $|...8\sigma^2 3\pi^4 1\delta^2 9\sigma^1|$ in the CASSCF wave function is close to 90% at the equilibrium distance.)

Vibrational frequencies calculated by the wave function based methods clearly demonstrate the well-known wisdom: they lead to good agreement between the calculated and experimental values of vibrational frequencies only if correlation effects are taken into account. The Hartree−Fock result is almost 300 cm^{-1} above the measured value. At the correlated level, the largest deviations of 50 cm^{-1} are found for the CISD and CPF results of Bauschlicher and Langhoff.[54] (The difference between the single reference (!) CISD and CPF results of these authors is conspicuously large and might be a manifestation of the need for multireference methods.)

Our work on the (well-studied) systems VO^+ and VO shows that extrapolation techniques are necessary if one wants to calculate highly accurate dissociation energies. For bond lengths, a consistent improvement over quite good density functional results is hard to obtain even by multireference methods. In contrary, vibrational frequencies seem to be more sensitive to the multiconfigurational character of the wave function. It should also be noted that good agreement of the density functional results for spectroscopic constants is often occasional and further proofs by more elaborated methods is needed.

TABLE 5: Calculated Properties of the VO Anion

method	R_e, Å	D_e, eV	D_0, eV	ω_e, cm^{-1}	ν_1, cm^{-1}	ref
MR-ACPF	1.626	5.63	5.59	957	953	this work
B3LYP	1.602	6.41	6.34	1028	1019	this work
BP86	1.607	7.42	7.38	1007	998	this work
B3LYP	1.61					16
BP86	1.62					16
BPW91	1.609			970		15
BLYP	1.619			960		15
B3LYP	1.604			991		15
exp.	$>R$(VO)			900 (±50)		7

4. Ground State Properties of the VO− Anion

In contrast to the neutral molecule VO and the cation VO^+, there are only few recent DFT studies of the VO anion.[15,16] The nature of the ground-state turns out to be ambiguous: theoretical studies have found a $^3\Sigma^-$ state, whereas Wu and Wang postulate a $^5\Pi$ state being based on PES measurements.[7]

We have performed both multireference ACPF and density functional calculations for the VO^- anion in order to get a “state of the art” theoretical description of its ground state. The results of these and previously published calculations are collected in the Table 5.

Bond distances calculated by different methods differ only by a few hundredth of Å. The MR-ACPF value reduces just slightly from 1.626 to 1.622 if we include correlation of the semicore 3s(V) and 3p(V) electrons. Thus, the equilibrium distance of the VO^- anion is 1.60−1.63 Å depending on the calculation.

To our knowledge, no binding energy of the VO^- anion has been published yet. MR-ACPF results for D_0 of the cation and neutral VO molecule presented earlier in this paper deviated by at most 0.1 eV from the measured values. For the anion, we expect an error of about the same size. This implies that our MR-ACPF value of 5.59 eV is a rather accurate estimate for the binding energy of VO^- and DFT methods considerably overestimate it. This is not too surprising, as density functional calculations quite generally have difficulties in describing small negative ions.

Vibrational frequencies have been already calculated by Gutsev et al.[15] and are by about 30−40 cm^{-1} smaller than our DFT values. All of the density functional results significantly overestimate the experimental value. As we already have shown for the cation and neutral molecule, DFT methods overestimate vibrational frequencies due to the single-reference formalism. The CASSCF wave function for the ground state of the VO^- anion at the equilibrium distance is dominated by the configuration $|...8\sigma^2 3\pi^4 9\sigma^2 1\delta^2|$ which has weight of 91%. In this case, multireference treatment would provide more accurate results as we have shown in sections 3.2 and 3.3. Our MR-ACPF value for ν_1 is rather close to the upper bound of the measured vibrational frequency. In view of the high accuracy that MR-ACPF results could reach for VO^+ and VO, we have some confidence in our theoretical value for the vibrational frequency of VO^-, too.

Finally, we point out that the ground state of the VO anion is $^3\Sigma^-$ rather than the $^5\Pi$ state which was experimentally postulated by Wu and Wang.[7] The assignment of the authors is based on the observation that the bond distance of the anion is larger than in the neutral molecule, accompanied by a red shift of the vibrational frequency from the neutral VO molecule to the anion. Wu and Wang argued that these features are due to the occupation of the antibonding 2 π^* orbitals, and the resulting ground state must be a $^5\Pi$. It is obvious, however, that all

TABLE 6: Results of the Population Analysis for the $VO^{+/0/-}$ Species

ground states		character of the MOs	
VO^+	$^3\Sigma^-$, $\|...8\sigma^2 3\pi^4 1\delta^2\|$[a]	8σ	$5 \times 2p_\sigma(O) + 1 \times 3d_\sigma(V)$
asymptotes		3π	$11 \times 2p_\pi(O) + 1 \times 3d_\pi(V)$
V^+	^5F,...$3d^4\ 4s^0$	1δ	$3d_\delta(V)$
O	^3P,...$2s^2 2p^4$		
VO	$^4\Sigma^-$, $\|...8\sigma^2 3\pi^4 1\delta^2 9\sigma^1\|$[a]	8σ	$5 \times 2p_\sigma(O) + 3 \times 3d_\sigma(V)$
asymptotes		3π	$11 \times 2p_\pi(O) + 1 \times 3d_\pi(V)$
V	^4F,...$3d^3\ 4s^2$	1δ	$3d_\delta(V)$
O	^3P,...$2s^2 2p^4$	9σ	$3d_\sigma(V)$
VO^-	$^3\Sigma^-$, $\|...8\sigma^2 3\pi^4 1\delta^2 9\sigma^2\|$[a]	8σ	$7 \times 2p_\sigma(O) + 1 \times 3d_\sigma(V) + 1 \times s(V)$
asymptotes		3π	$11 \times 2p_\pi(O) + 1 \times 3d_\pi(V)$
V	^4F,...$3d^3\ 4s^2$	1δ	$3d_\delta(V)$
O^-	^2P,...$2s^2 2p^5$	9σ	$17 \times 4s(V) + 2 \times s(O) + 1 \times 3d_\sigma(V)$

[a] Leading configuration.

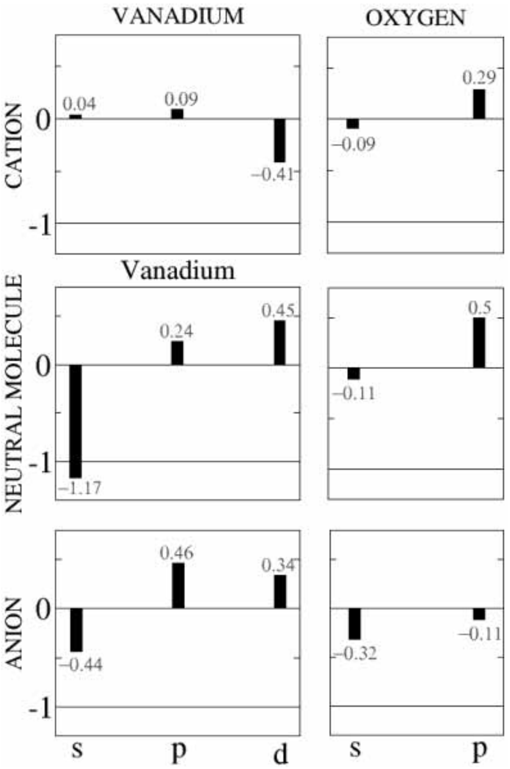

Figure 1. Differences of the Mulliken populations in the VO species compared to the corresponding asymptotic values ([V^+ +O], [V + O], and [V + O^-]) for the cation, neutral molecule, and anion, respectively.

observed features are compatible with the theoretically found $^3\Sigma^-$ ground state. The extra electron of the anion mainly occupies the 9σ orbital. The antibonding character of this orbital is already obvious if one compares the properties of the cation VO^+ with those of the neutral VO molecule.

We should also mention that our assignment of the VO^- ground state is in agreement with the previously published DFT studies.[15,16]

5. Population Analysis

The results of the Mulliken population analysis allows an insight into the distribution of the electron density over the atoms and bonds. We compare the atomic populations for the cation, neutral molecule, and anion with the corresponding asymptotic values ([V^+ + O], [V + O], and [V + O^-] for the cation, neutral molecule, and anion, respectively). Population differences between the bound systems and asymptotes are shown on the Figure 1 (results are obtained using cc-pVTZ basis). Additionally, we give in Table 6 the electronic structure of the ground state together with the composition of the highest occupied molecular orbitals.

If we built the VO^+ cation from its atomic asymptotes, V^+ and O, we observe a medium electron loss (less than 0.5) from the d(V) orbitals to the p(O) ones. Indeed, the doubly occupied bonding 8σ and 3π orbitals with a mainly $2p_\sigma(O)$ and $2p_\pi(O)$ character, respectively, have small contributions from the corresponding $3d_\sigma$ and $3d_\pi$ vanadium orbitals. This simple picture agrees also with the calculated charges which are +1.26 for the vanadium and −0.26 for the oxygen atom. The lack of significant change in the s(V) population implies a minor role of the 4s(V) orbital for the bonding in the VO^+ cation.

In the case of the neutral VO molecule, we see a large electron loss (more than 1) from the s(V) orbitals in favor of d(V), p(V), and p(O) ones. Obviously, the multireference character of the ground state is reflected in an increase of the p(V) and d(V) populations through the excited "s(V) → (p(V),d(V))" configurations. Calculated Mulliken charges are +0.45 and −0.45 for the vanadium and oxygen atom, respectively. Thus, the VO bond might be seen as partly ionic.

In the anion, we again observe significant contributions from excited s(V)−d(V) configurations as well as a small shift of electron density from s(O) to d(V) orbitals. This picture is, however, rather simplified. (For the population analysis, the cc-pVTZ basis was used although a basis set with diffuse functions (at least for oxygen) is needed for the more accurate description of the ground state of OV^-. However, Mulliken population analysis is known for getting somewhat arbitrary if diffuse functions are present.) Despite everything, we believe, that at least main features of the electron density distribution in the VO^- anion could be illustrated in our picture. Calculated atomic charges are −0.39 and −0.61 for vanadium and oxygen, respectively. This supports our assumption (see section 2.2) that the extra electron in the VO^- anion is preferably located at the oxygen site.

6. Ionic Properties of the VO Molecule

The first ionization potential (IP) and electron affinity (EA) of the VO molecule (see Table 7) turns out to be a challenge for theoretical methods. If we simply apply the MR-ACPF approach together with extrapolation of the correlation energy to the basis set limit, we get too small values for both IP and EA. Calculated ionization energies are almost independent from the kind of the transition and are by nearly 0.30 eV smaller than the measured value. Both a further inclusion of scalar relativistic corrections and taking into account correlation of the semicore 3s(V) and 3p(V) electrons increase the IP value by nearly the same amount (~0.1 eV). Such large corrections

TABLE 7: First Ionization Potential (IP) and Electron Affinity (EA) of the VO Molecule

method	transition			ref
	adiabatic	vertical	"0−0"	
	IP, eV			
MR-ACPF	6.95	6.97	6.95	this work
+rc[a]	7.06			this work
+scc[b]	7.05			this work
B3LYP	7.35 (7.34[c])			this work
BP86	7.54			this work
B3LYP	7.16			20
exp.		7.24		60
	EA, eV			
MR-ACPF	1.05	0.94	1.05	this work
+rc[a]	1.09			this work
+scc[b]	1.03			this work
B3LYP	0.72 (0.94[c])			this work
BP86	0.69			this work
B3LYP	1.09			15
BLYP	0.98			15
BPW91	0.81			15
B3LYP	0.86			16
BP86	0.83			16
exp.		1.21		7

[a] Including scalar relativistic corrections calculated using a) cc-pV5Z basis sets for both atoms to calculate the correction to IP, b) cc-pV5Z for the vanadium atom and aug-cc-pV5Z for the oxygen atom to calculate the correction to EA. [b] Including correction caused by semicore correlation calculated using our cc-pV5Z basis augmented with a set of tight p−h functions and fully decontracted p and d functions for the vanadium atom, aug-cc-CV5Z basis of Dunning for the oxygen atom. [c] Calculated using cc-pV5Z basis sets and equilibrium distances obtained by the corresponding method.

indicate the necessity of considering both effects together and in a more sophisticated way than done in our work.

MR-ACPF values for the electron affinity are also too small compared to the experiment. In contrary to the ionization potential, we do not find any large corrections to EA caused by relativistic effects or correlation of the semicore electrons. Furthermore, there is a relatively large difference (0.09 eV) between the adiabatic and vertical transition. The equilibrium bond distance in the neutral VO molecule is about 0.03 Å shorter than in the anion; that is, a vertical transition goes from the minimum on the potential energy curve of the neutral molecule to a point on the repulsive part of the potential energy curve of the anion. This leads the an decrease of the energy difference compared to the adiabatic transition. (This situation is opposite to the ionization where a vertical transition leads to the dissociative part of the potential energy curve of the cation which has a shorter bond distance than the neutral molecule. The slope of the dissociative part of the potential energy curve is smaller than the slope of the repulsive part. Therefore, the difference between a vertical and adiabatic transition from the neutral molecule to the cation is smaller than for the EA.)

This is some scatter within the density functional results for the ionization potential and electron affinity of VO, even between calculations with the same exchange-correlation functional. This might indicate that, for density functional calculations, basis sets beyond triple-ζ quality are required to get convergent results. (For instance, our B3LYP values for EA changes significantly going from the cc-pVTZ to the cc-pV5Z basis.) Alhough most of the calculated IP values deviate only by 0.1 eV from the experimental value, DFT results for EA are by 0.2−0.4 eV too small independently from the exchange-correlation functional and basis set. Probably large errors of the calculated binding energies for the VO$^-$ anion by DFT methods (see section 5) and poor density functional results for the electron affinity of VO have the same reasons.

Assuming additivity of relativistic effects and correction due to semicore correlation, our final estimates are 7.16 for IP and 1.07 eV for EA. They are still 0.08 and 0.14 eV, respectively, smaller than corresponding experimental values. Recalling that standard theoretical methods predict electron affinities with an error of about 0.2 eV for molecules consisting of main group elements,[61] it becomes clear that obtaining accurate thermodynamical data on transition metal compounds by theoretical methods is still a difficult task. It is also worth it to check whether augmented basis sets for the vanadium atom (which has not been constructed yet) would improve results of the calculation significantly.

7. Conclusions

We have presented "state of the art" calculations for the ground states of the cationic, neutral, and anionic VO species. Correlation consistent basis sets for the vanadium atom generated in this study work well with the Truhlar's extrapolation technique and have enabled us to obtain highly accurate theoretical results for the spectroscopic properties of the studied systems. Density functional calculations generally show satisfactory agreement with our ab initio results and experimental data although statistical rather than systematic error distributions have been observed. Finally, our assignment of the ground state of the VO$^-$ anion ($^3\Sigma^-$) agrees with the previous DFT studies, such that theory unambiguously rejects the experimental assignment ($^5\Pi$).

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Supporting Information Available: The vanadium basis sets of double-ζ (DZ) through quintuple-ζ (5Z) quality that have been constructed in the course of this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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