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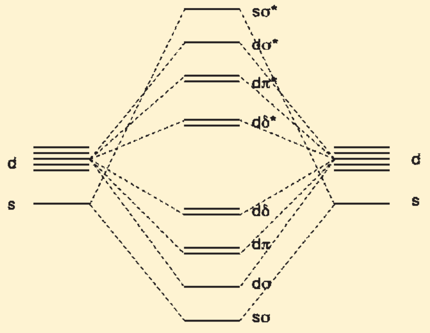
Electronic Structure and Bonding in Heteronuclear Dimers of V, Cr, Mo, and W: a CASSCF/CASPT2 Study

Fernando Ruipérez, Jesus M. Ugalde, and Ivan Infante*

Kimika Fakultatea, Euskal Herriko Unibertsitatea and Donostia International Physics Center (DIPC), P. K. 1072, 20080 Donostia, Euskadi, Spain

S Supporting Information

ABSTRACT: Heteronuclear dimers like CrMo, CrW, MoW, VCr, VMo, VW, and their anions have been investigated by means of multiconfigurational quantum chemistry methods, using the complete active space self-consistent field followed by second-order perturbation theory, CASSCF/CASPT2. We explored in great detail several spectroscopic properties such as bond length, potential energy surfaces, dissociation energies, ionization potentials, electron affinities, low-lying excited states, vibrational frequencies, and dipole moments. All proposed dimers show ground states with a pronounced multireference character. The group VI heterodimers have a ${}^1\Sigma^+$ ground state, while the mixed group V−group VI heterodimers show a ${}^2\Delta$ ground state. Among all dimers, only VCr presents a potential energy profile with a deep minimum in the d−d region and a shelf-like potential in the s−s region. All the remaining dimers show only the short-range minimum. The largest effective bond order is obtained for the MoW, with a value of 5.2, that is, a weak sextuple bond. Most of the obtained results are valuable tools to drive future experimental investigations.



1. INTRODUCTION

The research carried out on nanoclusters is essential nowadays in science and technology as they serve as a bridge between bulk materials, like nanomaterials, and atomic structures. These nanoclusters are composed of nanoparticles that in some cases can be either homonuclear clusters or heteroatomic structures, in which the coexistence of different type of metals may give rise to interesting electronic, structural, chemical, or catalytic properties. The study of the chemical bond of small metal clusters is a crucial issue to understand and predict the behavior of nanomaterials of more realistic sizes.

Our focus on such small metal clusters is based on the assumption that both experimental and theoretical analyses are somewhat facilitated and, in particular, the study of metal dimers allows an in-depth analysis of their molecular properties without the presence of ligands that might complicate the interpretation of the experimental results and, at the same time, relieves the computational effort needed to describe them. During the past years, experimental work has been carried out on homonuclear diatomic molecules of groups V and VI, in gas phase or in matrixes, using techniques such as negative ion photoelectron spectroscopy or resonant two-photon ionization (R2PI).[1−5] In contrast, rather little is known about the dimers of the mixed V/VI groups.

In this work we aim to study heteronuclear dimers constituted by the elements of group VI, Cr, Mo, and W, and vanadium from group V. Group VI metals have been studied before, and the bonding and electronic properties of the *homonuclear* dimers, Cr_2,[6−8] Mo_2,[9,10] and W_2,[11,12] have been characterized experimentally and theoretically. Despite this, *heteronuclear* dimers of the same group are only little studied, and the only available information, to our knowledge, corresponds to the CrMo molecule.[1,13] Regarding vanadium, a couple of studies have been performed for both the homonuclear dimer, V_2,[14,15] and the heteronuclear molecules such as VMo[4] and VCr.[2,16] Another important point to consider is that the chromium dimer, Cr_2, shows one of the most complicated chemical bonds among homonuclear metal dimers[7,8,17] throughout the whole periodic table, and it is therefore very appealing to assess how such a bond is modified when one of the chromium atoms is attached to V, Mo, or W.

In this work we perform an ab initio theoretical study of the transition metal dimers CrMo, CrW, MoW, VCr, VMo, and VW to achieve a better understanding of their electronic structure and bonding properties and provide data that could be useful in future experimental investigations.

It is well-known that the chemical bond in transition metals involves the five nd and the $(n + 1)$s orbitals; however, in the early metals, the bond occurs in the d−d region in contrast to the bond in the late metals that is dominated by a s−s bond, partly because of filling and consequent contraction of the d orbitals relative to the s orbitals. From a theoretical point of view, the description of these heterodimers presents difficulties for several reasons: the partially occupied d orbitals give rise to dense manifolds of low-lying excited states and multireference wave functions are required to provide a qualitative account of the correct ground

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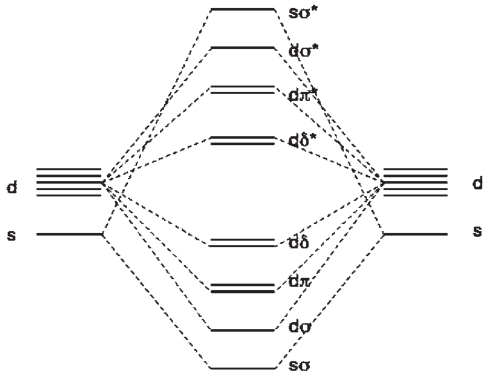

Figure 1. Schematic view of the molecular orbitals inside the active space, generated from the linear combination of the atomic *n*d and (*n* + 1)s atomic orbitals. The position of the s orbitals relative to the d orbitals changes depending on the atom.

state electronic structure and dissociation energies. Moreover, both static and dynamic correlation are necessary to provide an accurate description of the potential energy surfaces (PESs). Finally, in some cases like the Cr_2 dimer, two bond regions may exist along the PES because of the distinct d−d and s−s interactions.

On the basis of these arguments, we decided to analyze these heteronuclear dimers using the CASSCF/CASPT2 method that has been proven in the past to accurately describe similar molecules characterized by a heavy multireference character, large dynamic correlation energy, and significant relativistic effects.

2. DETAILS OF THE CALCULATIONS

Spin-free calculations were performed at the all-electron level with scalar relativistic effects included through the second-order Douglas−Kroll−Hess Hamiltonian.[18,19] The wave functions were obtained by means of complete active space self-consistent field calculations (CASSCF),[20] where the active space is defined by the distribution of 12 electrons in 12 molecular orbitals composed of the *n*d and (*n* + 1)s atomic orbitals (see Figure 1). Dynamic correlation is taken into account through complete active space second-order perturbation theory calculations (CASPT2)[21,22] using the ionization potential electron affinity (IPEA)-corrected zeroth-order Hamiltonian,[23] with the default value of $\varepsilon = 0.25$ for the IPEA shift. The imaginary shift technique[24] was used to achieve convergence and avoid the presence of intruder states in the CASPT2 step, where the *n*s and *n*p atomic orbitals are also correlated dynamically, as well as the 4f shell in the case of tungsten atom. The value of the imaginary shift employed in this work was 0.20 au. Spin−orbit coupling (SO) calculations were carried out using the CASPT2-corrected restricted active space state-interaction with the spin−orbit coupling method RASSI-SO.[25] To include the dynamic correlation effects in the spin−orbit calculations, an effective Hamiltonian is defined where the diagonal matrix elements are shifted using the energy differences between the CASSCF and CASPT2 values.[26,27] Spectroscopic constants from the PESs were obtained with the program VIBROT implemented in MOLCAS.[28] We have used the all-electron atomic natural orbitals (ANO-RCC) basis sets of quadruple-ζ size for all atoms.[29]

In some cases following the dissociation channel does not lead to the lowest dissociation energy, that is, at the asymptotic limit one or both atoms may be in one of their excited states. Hence, we give two types of dissociation energies, one relative to the dissociation channel, D_e, as given by VIBROT and one for the lowest dissociation energy, D'_e, computed as the energy difference between the dimer at the equilibrium and the isolated atoms in their ground state. Experimental techniques might employ either way to measure this dissociation. These values have been corrected using counterpoise correction.[30]

All the spectroscopic constants have been computed at the spin-free level. An exception is represented by the dimers including the W atom: CrW, MoW, and VW. Indeed, the W atom exhibits strong relativistic effects; hence the spin−orbit coupling is mandatory in the calculations. There are two ways we could include this effect: one is to compute the spin−orbit term on each point of the PES, then using VIBROT to compute the spectroscopic parameters; the other is to optimize the geometry at spin-free level, and then to compute the spin−orbit coupling a posteriori, as a single point on the optimized structure (and on the isolated atoms for the dissociation energy), to evaluate the spectroscopic parameters. For its simplicity and also for computational time, we decided for the latter way; hence, we provided spin-free D_e, R_e, $\Delta G_{1/2}$ and spin−orbit D'_e, ionization potential and electron affinity. In any cases, for all dimers, the excited states have been computed with the inclusion of the spin−orbit term.

All calculations were performed using C_1 point symmetry groups although the actual symmetry of the heterodimers is $C_{\infty v}$. Unfortunately, the employment of non-abelian groups with degenerate irreducible representations is not implemented in MOLCAS 7.4.,[28] the program package we have used in this work. We noticed that using symmetry higher than C_1 can lead to some problems, for example, when a pair of degenerate states is split into two distinct irreducible representations (like in the C_{2v} case). In a state-average calculation, like the one employed in this work, this could bring about a spurious energy difference between two degenerate states, and such a difference in some cases may be quite large. Hence, we decided to remove the use of symmetry in the calculations, using the C_1 point group, so that the degenerate pair would always be correctly averaged. However, throughout the paper, we have used the electronic terms of the "real" symmetry, $C_{\infty v}$.

Under this framework, for the neutral dimers of group VI, we averaged 10 singlet states and 10 triplet states, for a total of 20 excited states mixed perturbatively to add the spin−orbit coupling using the RASSI approach, as mentioned earlier. For the heterodimers with vanadium, we have averaged 20 singlet and 20 triplet states (vanadium generates a larger number of low energy excited states). For all the anions we averaged 10 doublet states and 10 quartet states. This ensures that in any case we explore the excitation energies up to about 25000−30000 cm^{-1}. Furthermore, all the excited states have been computed at the geometry of the optimized spin-free ground state of a given species. This implies that all excitation energies are vertical and that spin−orbit is used to correct the energy and not the geometry of the ground and excited states.

Finally, the calculation of the force constants, *k*, has been performed using the computed fundamental vibrational frequencies, $\Delta G_{1/2}$, and the following isotopes: 51 for vanadium, 52 for chromium, 92 for molybdenum, and 184 for tungsten.

3. RESULTS

In this work we perform a study of the neutral heterodimers CrMo, CrW, MoW, VCr, VMo, and VW, as well as their corresponding anions. Since many of the experimental data on gas-phase metal dimers are obtained using negative ion photoelectron spectroscopy, the availability of theoretical data for the anions is useful to provide a more complete set of data. Sixty points along the PESs are computed for the ground state of each dimer up to 10.0 Å to get the spectroscopic constants: dissociation energies (D_e, D_0, and D'_e), equilibrium bond length (R_e), fundamental vibrational frequency ($\Delta G_{1/2}$), ionization potentials and electron affinities. To study the multiplicity of the chemical bond, we use the effective bond order (EBO),[31,32] defined as $\sum (\eta_b - \eta_{ab})/2$, where η_b and η_{ab} state for the natural orbital occupation of the bonding and antibonding orbitals,

Table 1. Spectroscopic Constants for CrMo and CrMo$^-$ Computed at the CASSCF/CASPT2 Level of Theory[a]

	R_e	$\Delta G_{1/2}$	D_e	D_0	D'_e	IP	EA	μ
CrMo	1.859	419	2.63	2.60	2.62	8.06	0.25	0.37
exp.	1.818[b]							
calc.[c]	1.840	449	2.09					
CrMo$^-$	1.866	402	2.66	2.63		0.25		

[a] Bond lengths are given in Å; vibrational frequencies in cm^{-1}; energies in eV. D_e and D_0 are obtained following the dissociation channel along the PES. D'_e is calculated using the isolated atoms in their ground states. Dipole moment (μ) in Debye. [b] Ref 1. [c] SC-NEVPT3 from 34.

respectively. Thus, the EBO is calculated for each pair of bonding—antibonding orbitals, and the total multiplicity of the bond will be given by the sum of all the individual EBO contributions. This EBO is a noninteger number and one should use the lowest integer value larger than the EBO obtained to define the multiplicity of the bond. However, the EBO concept works well for homonuclear dimers, while for heteronuclear dimers the ionicity of the bond, that is, the different electronegativity of the two metals, may play a significant role in defining the strength of the bond. This effect is not taken into account in the actual definition of the EBO; hence, it may be possible to have dimers with lower EBO and higher dissociation energy.

3.1. Group VI Heterodimers.

3.1.1. CrMo. The ground state for both chromium and molybdenum atoms is a $^7S_3$[33] arising from the electronic configurations $3d^5(^6S)4s^1$ of Cr and $4d^5(^6S)5s^1$ of Mo. The molecular ground state for the neutral molecule is computed to be a singlet $^1\Sigma^+$ with a dominant electronic configuration of $|d\sigma^2 d\pi^4 d\delta^4 s\sigma^2\rangle$, whose weight is only 52% of the total wave function. This rather multiconfigurational ground state is expected if compared to the chromium dimer that exhibits even a more pronounced multireference character (47%).[6,7,17] The calculated spectroscopic constants for the CrMo ground state correspond to an equilibrium bond length of R_e = 1.859 Å, a vibrational frequency of $\Delta G_{1/2}$ = 419 cm^{-1}, and a dissociation energy of D_e = 2.63 eV (D_0 = 2.60 eV). The dissociation energy obtained from the isolated atoms in their ground state is basically the same, D'_e = 2.62 eV, see Table 1. The calculated ionization potential and electron affinity are 8.06 and 0.25 eV, respectively. No experimental vibrational frequency or dissociation energy are available; however, the equilibrium bond length was measured, 1.818 Å,[1] and is in fair agreement with our value. Previous calculations[34] in this molecule obtained the following spectroscopic constants: R_e = 1.840 Å and $\Delta G_{1/2}$ = 449 cm^{-1}. The shape of the PES at the CASSCF level shows one minimum at short distance and a shelf-like potential at larger distances, however, this feature disappears after including the dynamic correlation, in the CASPT2 step.

Although the atomic ground states of Cr and Mo, with six unpaired electrons, would allow the existence of a sextuple bond, it is observed that the occupation of antibonding dδ* and dπ* orbitals significantly weakens the bond. The calculated occupation numbers of the CASSCF natural orbitals are indeed the following: $(s\sigma)^{1.90}$ $(d\sigma)^{1.82}$ $(d\pi)^{3.69}$ $(d\delta)^{3.29}$ $(s\sigma^*)^{0.10}$ $(d\sigma^*)^{0.18}$ $(d\pi^*)^{0.31}$ $(d\delta^*)^{0.71}$. Thus, the EBO is 4.70, which means a quintuple bond. The calculated dipole moment is μ = 0.37 D, as a consequence of a small charge transfer of 0.04e from Cr to Mo.

Regarding the electronic structure of the anion, CrMo$^-$, the extra electron is located in the sσ* orbital, giving rise to a $^2\Sigma^+$ state with the following ground state electronic configuration: $|\Psi_{^2\Sigma^+}\rangle$ = 0.56 $|d\sigma^2 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1\rangle$. The occupation numbers of the natural orbitals for the anion are $(s\sigma)^{1.99}$ $(d\sigma)^{1.82}$ $(d\pi)^{3.70}$ $(d\delta)^{3.34}$ $(s\sigma^*)^{1.01}$ $(d\sigma^*)^{0.17}$ $(d\pi^*)^{0.30}$ $(d\delta^*)^{0.66}$ and the calculated EBO is 4.35 that can be considered also as a quintuple bond but less strong as compared to the neutral molecule (EBO = 4.70). This is expected because of the population of the antibonding sσ* orbital. The equilibrium bond length is R_e = 1.866 Å and the vibrational frequency is $\Delta G_{1/2}$ = 402 cm^{-1}, showing only a small difference with the neutral molecule. This fact is also reflected in the dissociation energy, D_e = 2.66 eV (D_0 = 2.63 eV) which is slightly larger than the one of the neutral CrMo (D_e = 2.63 eV and D_0 = 2.60) although an antibonding orbital, sσ*, is populated in the anion.

Excited States. We have calculated vertical excited states for neutral CrMo up to 30000 cm^{-1} including spin—orbit coupling. In Table 2 are collected the configurations, the type of the excitation, and the energies for each excited state. The first two excited states, at 7339 cm^{-1} and 7395 cm^{-1}, correspond to the spin—orbit splitting of the $^3\Sigma^+$ level, which involves an excitation from the bonding dδ to the corresponding antibonding dδ*. On the other side, the excitation from the bonding sσ to the antibonding sσ* gives rise to another $^3\Sigma^+$ level, which is split by spin—orbit coupling into two states at 14675 and 14688 cm^{-1}. As it is easily noticed, the SO effect is very small, and a spin-free analysis would vary very little from the most complete SO results. The excited states up to about 20000 cm^{-1} are of little interest, since their oscillator strength is approximately zero. On the other side, one of the most intense transition is given by the $^1\Sigma^+$ to $^1\Sigma^+$ excitation, which in our calculations appears at 22420 cm^{-1} and compares well with the same transition reported experimentally at 20527 cm^{-1}.[1] Another very intense transition lies at 24600 cm^{-1}; however, this has not been identified experimentally yet, and its finding may represent a litmus test for the reliability of our theoretical approach.

3.1.2. CrW. The calculated ground state of neutral CrW is a singlet $^1\Sigma^+$ with the following dominant electronic configuration: $|\Psi_{^1\Sigma^+}\rangle$ = 0.50 $|d\sigma^2 d\pi^4 d\delta^4 s\sigma^2\rangle$. As we previously observed in CrMo, this ground state reveals a pronounced multiconfigurational nature. As we have also found in CrMo, the spin-free PES exhibits two minima at the CASSCF level but only one when the dynamic correlation is included through the CASPT2 calculations. The spin-free spectroscopic constants obtained are then the following: equilibrium bond length, R_e = 1.919 Å, vibrational frequency, $\Delta G_{1/2}$ = 348 cm^{-1}, dissociation energy, D_e = 3.19 eV (D_0 = 3.17 eV), and the dipole moment, μ = 0.98 (in this case the charge transfer of about 0.11e occurs from W to Cr). We have also calculated the spin—orbit ionization potential, IP = 6.75 eV, and the electron affinity, EA = 0.42 eV. For the computation of spin—orbit D'_e the situation is somewhat more complicated. Indeed, the simple (6,6) active space is not able to reproduce the correct ground state for the W atom. To overcome this, we had to add explicitly the 6d orbitals in the CAS inducing, unfortunately, an imbalance for the computation of the dissociation energy at CASSCF level. To restore the numerical size-consistency, in the CASPT2 step we included the 3s and 3p and all virtual orbitals. This does not exclude errors on the evaluation of the D'_e, because of the possibility that the perturbation theory is not sufficiently accurate to recover successfully the dynamic correlation energy. Because of this, the computed value of 2.73 eV for the CrW must be considered with care (see Table 3).

The ground state of the isolated atoms[33] are Cr, $3d^5 4s^1 (^7S_3)$, and W, $5d^4 6s^2 (^5D_0)$, which in principle would allow at most a

Table 2. Low-Lying Vertical Excited States for Neutral CrMo Including Spin-Orbit Coupling[a]

state	SF levels	configuration	excitation	ΔE_{SF}	ΔE_{SO}	f
0	$A^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^2$		0	0	
1	$A^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	dδ → dδ*	7386	7339	0
0					7395	0
1	$B^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^1 (s\sigma^*)^1$	sσ → sσ*	14678	14675	0
0					14688	0
4	$A^3\Gamma$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	dδ → dδ*	15762	15699	0
3					15747	0
5					15796	0
3	$A^3\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	dδ → sσ*	17405	17101	0
2					17342	0
1					17731	0
0	$C^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	dδ → dδ*	18140	18157	0
1					18217	0
2	$A^1\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	dδ → sσ*	18785	18868	0
0	$B^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	dδ → dδ*	20362	20371	0
1	$D^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (d\delta^*)^1 (s\sigma^*)^1$	dδ → dδ*	22292	22302	0
0			sσ → sσ*		22302	0
0	$C^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (d\delta^*)^1 (s\sigma^*)^1$	dδ → dδ*	22410	22420	0.1419
			sσ → sσ*	(20527)	(20527)	
4	$A^1\Gamma$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	dδ → dδ*	22713	22731	0.00034
0	$D^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$ +	dδ → dδ*	24590	24600	0.3002
		$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	dδ → sσ*			
4	$B^3\Gamma$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^2$	dδ → dδ*	24623	24627	0
3					24637	0
5					24695	0
0	$E^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^2$	dδ → dδ*	25805	25814	0.00031
0	$F^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (d\delta^*)^1 (s\sigma^*)^1$	sσ → sσ*	27712	27721	0.00346
			dδ → dδ*			

[a] The main spin-free contributions are given in the second column. Relative energies (ΔE_{SF}) and (ΔE_{SO}) are in cm^{-1}. f is the oscillator strength. The (ΔE_{SF}) are not averaged energies of the spin-orbit values, but are taken from the actual spin-free calculation. The experimental value is given in parentheses[1].

Table 3. Spectroscopic Constants for CrW and CrW$^-$ Computed at the CASSCF/CASPT2 Level of Theory[a]

	R_e[b]	$\Delta G_{1/2}$[b]	D_e[b]	D_0[b]	D'_e[c]	IP[c]	EA[c]	μ[b]
CrW	1.919	348	3.19	3.17	2.73	6.75	0.42	0.98
CrW$^-$	1.965	287	2.90	2.89		0.42		

[a] Bond lengths are given in Å; vibrational frequencies in cm^{-1}; energies in eV. D_e and D_0 are obtained following the dissociation channel along the PES. D'_e is calculated using the isolated atoms in their ground states. Dipole moment (μ) in Debye. [b] Spin-free. [c] Spin−orbit.

quadruple bond for the CrW dimer. The Cr atom, however, induces on the W atom the promotion of one electron from the doubly occupied 6s orbital to one of the empty 5d orbitals, allowing a higher bond multiplicity when the two metals approach each other. The natural orbital occupation is: $(s\sigma)^{1.91}$ $(d\sigma)^{1.82}$ $(d\pi)^{3.70}$ $(d\delta)^{2.93}$ $(s\sigma^*)^{0.58}$ $(d\sigma^*)^{0.17}$ $(d\pi^*)^{0.30}$ $(d\delta^*)^{0.58}$ and the calculated EBO is 4.37, that is, a quintuple bond.

To our knowledge, no experimental values are reported for this system.

The ground state of the anion, CrW$^-$, is a doublet $^2\Sigma^+$, with an unpaired electron in the antibonding sσ* orbital. The corresponding electronic configuration, $|\Psi_{^2\Sigma^+}\rangle = 0.53\,|d\sigma^2 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1\rangle$, shows also a clear multireference character. The bond length is 1.965 Å, the vibrational frequency is 287 cm^{-1}, and the spin-free dissociation energy is $D_e = 2.90$ eV. This molecule shows a weak quintuple bond with an EBO of 4.11, which is calculated from the following natural orbital occupation: $(s\sigma)^{1.99}$ $(d\sigma)^{1.60}$ $(d\pi)^{3.68}$ $(d\delta)^{3.23}$ $(s\sigma^*)^{1.01}$ $(d\sigma^*)^{0.19}$ $(d\pi^*)^{0.32}$ $(d\delta^*)^{0.74}$. In this case, the bond is weakened compared to the neutral CrW, most probably because of the extra electron occupying the antibonding sσ* orbital.

Excited States. We have examined the excited states of the CrW dimer up to 30000 cm^{-1} including spin−orbit coupling (Table 4). The first two states at 8634 cm^{-1} correspond to the spin−orbit splitting of the first spin-free $^3\Sigma^+$ level, which is represented by an excitation from the dδ orbital to the antibonding dδ*. The next three states are generated by the spin−orbit splitting of the $^3\Delta$ spin-free level, ranging from 11649 to 13554 cm^{-1}, and based on excitations to the antibonding sσ* orbital. Finally, we have included the intense singlet-to-singlet transition, which involves and excitation from the sσ orbital to the antibonding sσ* (and also from the dσ orbital to the antibonding sσ*). This excitation lies at 24751 cm^{-1} and may be used as reference for eventual experimental measurement. There is also another state that is UV-active, about 10 times less intense, that lies at 21663 cm^{-1}.

3.1.3. MoW. Neutral MoW exhibits a singlet ground state, $^1\Sigma^+$, with the following dominant electronic configuration:

Table 4. Low-Lying Vertical Excited States for Neutral CrW Including Spin-Orbit Coupling[a]

state	SF levels	configuration	excitation	ΔE_{SF}	ΔE_{SO}	f
0	$A^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^2$		0	0	0
1	$A^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	8634	8634	0
0					8634	0
3	$A^3\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	12661	11649	0
2					12216	0
1					13554	0
2	$A^1\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	14479	14697	0
1	$B^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	16692	16692	0
0					16692	0
0	$C^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$	18144	18107	0
1					18144	0
1	$A^1\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	20550	20570	0
1	$B^3\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	21741	20417	0
2			$d\delta \rightarrow d\delta^*$		21236	0
3					21260	0
3	$C^3\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1 (s\sigma^*)^1$	$d\delta \rightarrow d\delta^*$	20955	20636	0
2			$d\delta \rightarrow s\sigma^*$		20765	0
1					21311	0
1	$D^3\Sigma^+$	$d\sigma^1 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1$	$d\sigma \rightarrow s\sigma^*$	21190	21121	0
0					21190	0
0	$B^1\Sigma^+$	$d\sigma^1 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1$	$d\sigma \rightarrow s\sigma^*$	21663	21663	0.0106
2	$B^1\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1 (s\sigma^*)^1$	$d\delta \rightarrow d\delta^*$ $d\delta \rightarrow s\sigma^*$	22734	23627	0
0	$C^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^1 (s\sigma^*)^1$ + $d\sigma^1 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$ $d\sigma \rightarrow s\sigma^*$	24751	24751	0.1839
1	$A^1\Pi$	$d\sigma^2 d\pi^3 d\delta^4 s\sigma^2 (s\sigma^*)^1$	$d\pi \rightarrow s\sigma^*$	25515	25656	0.001

[a] The main spin-free contributions are given in the second column. Relative energies (ΔE_{SF}) and (ΔE_{SO}) are in cm^{-1}. f is the oscillator strength. The (ΔE_{SF}) are not averaged energies of the spin-orbit values, but are taken from the actual spin-free calculation.

Table 5. Spectroscopic Constants for MoW and MoW$^-$ Computed at the CASSCF/CASPT2 Level of Theory[a]

	R_e[b]	$\Delta G_{1/2}$[b]	D_e[b]	D_0[b]	D'_e[c]	IP[c]	EA[c]	μ[b]
MoW	1.992	414	5.41	5.38	4.92	7.52	0.58	1.41
MoW$^-$	2.012	390	5.23	5.21		0.58		

[a] Bond lengths are given in Å; vibrational frequencies in cm^{-1}; energies in eV. D_e and D_0 are obtained following the dissociation channel along the PES. D'_e is calculated using the isolated atoms in their ground states. Dipole moment (μ) in Debye. [b] Spin-free. [c] Spin−orbit.

$|\Psi_{^1\Sigma^+}\rangle = 0.67|d\sigma^2 d\pi^4 d\delta^4 s\sigma^2\rangle$. Although this state has an important multiconfigurational nature, its effect is reduced with respect to CrMo (0.52) and CrW (0.50). This can be ascribed to the much stronger interaction between the Mo and W atoms that favors the expansion of the bonding/antibonding energy gap that in turn decreases the antibonding contribution to the total ground state wave function.

As explained in the case of CrW, the PES has been calculated at the spin-free level, obtaining the following spectroscopic constants (see Table 5): equilibrium bond length R_e = 1.992 Å, vibrational frequency $\Delta G_{1/2}$ = 414 cm^{-1}, and dissociation energy D_e = 5.41 eV (D_0 = 5.38 eV). The spin−orbit has been added to correct the dissociation, D'_e = 4.92 eV, the ionization potential, 7.52 eV, and the electron affinity, 0.58 eV. The spin-free dipole moment is 1.41 D, indicating the Mo to be significantly more negative, being capable of receiving 0.15e from W. For this dimer, for both the CASSCF and the CASPT2 PESs, only the minimum at short-range is observed while the shelf-like potential at long distance does not appear.

To our knowledge, no experimental values for this molecule are reported.

The ground states of the isolated atoms are W, 5d^{4}6s^2($^5D_0$), and Mo, 4d^{5}5s^1($^7S_3$), which would favor in principle a maximum multiplicity of four for the molybdenum−tungsten bond; however, analyzing the natural occupation number of MoW molecular orbitals, $(s\sigma)^{1.93}$ $(d\sigma)^{1.88}$ $(d\pi)^{3.81}$ $(d\delta)^{3.55}$ $(s\sigma^*)^{0.07}$ $(d\sigma^*)^{0.12}$ $(d\pi^*)^{0.19}$ $(d\delta^*)^{0.45}$, we find that the calculated EBO is 5.17, that is, a weak sextuple bond. As in case of CrW, the tungsten atom promotes one electron from the 6s orbital to one of the empty 5d orbitals and gives rise to one of the highest EBOs, probably the highest among all heteronuclear dimers.

The ground state of the anion, MoW$^-$, is a doublet $^2\Sigma^+$, where the extra electron is located in the antibonding sσ^* orbital. The dominant electronic configuration corresponding to this ground state is the following: $|\Psi_{^2\Sigma^+}\rangle = 0.71\ |d\sigma^2 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1\rangle$, and the calculated EBO for this molecule is 4.72, obtained from the occupation of the orbitals: $(s\sigma)^{1.88}(d\sigma)^{1.89}$ $(d\pi)^{3.81}$ $(d\delta)^{3.58}$ $(s\sigma^*)^{1.01}$ $(d\sigma^*)^{0.11}$ $(d\pi^*)^{0.19}$ $(d\delta^*)^{0.42}$. Thus, the anion has a quintuple bond. This weakening of the bond is probably due, as we found in some of the previously studied dimers, to the population of the antibonding sσ^* orbital. The equilibrium bond length is 2.012 Å, the vibrational frequency is 390 cm^{-1} and the spin-free dissociation energy is D_e = 5.23 eV (D_0 = 5.21 eV).

Excited States. The low-lying vertical excited states of neutral MoW up to 30000 cm^{-1}, including spin−orbit coupling, are listed in Table 6. The first two excited states, at 10937 and 11639 cm^{-1}, are the spin−orbit components of the spin-free $^3\Sigma^+$ level. This state lies at higher energies compared to CrMo and CrW. The first moderately intense transition is from the A$^1\Sigma^+$ to the C$^3\Sigma^+$ state and lies at 19680 cm^{-1}. The most intense transition is, as in the case of CrMo and CrW, a singlet-to-singlet transition that involves an excitation from the bonding sσ to the antibonding sσ^* orbitals. The energy of this excited state is 22558 cm^{-1}, which is quite similar to the other heterodimers seen so far. An eventual experimental measurement could use this region to find a strong signal.

3.2. Mixed Group V - Group VI Heterodimers.

3.2.1. VCr. This molecule is formed by a metal of group V (vanadium) with a metal of group VI (chromium) that combine to yield a doublet $^2\Delta$ ground state with a dominant electronic configuration, $|\Psi_{^2\Delta}\rangle = 0.52|d\sigma^2 d\pi^4 d\delta^3 s\sigma^2\rangle$, of notable multireference character. The inspection of the potential surface, both at the CASSCF and CASPT2 levels of theory, reveals the existence of a short-range minimum and a shelf-like potential at longer bond distances, as found for the Cr$_2$ dimer. The calculated spectroscopic constants of the ground state are the following (see Table 7): bond length, R_e = 1.736 Å, vibrational frequency, $\Delta G_{1/2}$ = 680 cm^{-1}, and the dissociation energy with respect to the isolated atoms, D'_e = 1.78 eV. The D_e is somewhat different, 2.19 eV (D_0 = 2.15 eV), since the dissociation channel leads to an excited state of the vanadium atom, hence to a higher dissociation energy.

Regarding the D_e, only a theoretical estimate[16] is available in the literature, namely, 2.262 eV, which is not far from the theoretical

Table 6. Low-Lying Vertical Excited States for Neutral MoW Including Spin-Orbit Coupling[a]

state	SF levels	configuration	excitation	ΔE_{SF}	ΔE_{SO}	f
0	$A^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^2$		0	0	0
1	$A^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	11528	10937	0
0					11639	0
3	$A^3\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	14395	13408	0
2					14072	0
1					15626	0
4	$A^3\Gamma$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	17442	16324	0
3					17255	0
5					17872	0
2	$A^1\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	16462	17028	0
1	$B^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$	19251	19008	0
0					19362	0
0	$C^3\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	19458	19680	0.0029
1					20640	0
0	$B^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	20050	20194	0
0	$C^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$	22414	22558	0.3046
4	$B^1\Gamma$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	21847	23053	0
0	$D^3\Sigma^+$	$d\sigma^1 d\pi^4 d\delta^4 s\sigma^2 (s\sigma^*)^1$	$d\sigma \rightarrow s\sigma^*$	26511	26632	0
1					26650	0
2	$B^1\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (s\sigma^*)^1 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$ $d\delta \rightarrow s\sigma^*$	27725	27850	0
3	$B^3\Gamma$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^2$	$d\delta \rightarrow d\delta^*$	28622	28741	0
5			$d\delta \rightarrow d\delta^*$		28749	0
4					28901	0
0	$D^1\Sigma^+$	$d\sigma^2 d\pi^4 d\delta^4 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$	29222	29345	0.0038

[a] The main spin-free contributions are given in the second column. Relative energies (ΔE_{SF}) and (ΔE_{SO}) are in cm^{-1}. f is the oscillator strength. The (ΔE_{SF}) are not averaged energies of the spin-orbit values, but are taken from the actual spin-free calculation.

Table 7. Spectroscopic Constants for VCr and VCr$^-$ Computed at the CASSCF/CASPT2 Level of Theory[a]

	R_e	$\Delta G_{1/2}$	D_e	D_0	D'_e	IP	EA	μ
VCr	1.736	680	2.19	2.15	1.78	6.03	0.88	0.91
exp.	1.7260[b]	505[c]					0.521[c]	
calc.[d]	1.720	557	2.262					
VCr$^-$	1.745	652	2.03	1.99		0.88		
exp.		406[c]						

[a] Bond lengths are given in Å; vibrational frequencies in cm^{-1}; energies in eV. D_e and D_0 are obtained following the dissociation channel along the PES. D'_e is calculated using the isolated atoms in their ground states. Dipole moment (μ) in Debye. [b] Ref 2. [c] Ref 3, preliminary results. [d] Ref 16, theoretical estimation.

value obtained here, 2.19 eV. The major difference with the earlier work lies on the vibrational frequency that Andersson computes at 557 cm^{-1}, about 100 cm^{-1} lower than our result. It should be noted, however, that the CASPT2 calculations performed by Andersson are different from the ones performed in this work. First, the so-called g1 zeroth-order Hamiltonian[35] was used in their work and the 3s and 3p shells were excluded in the dynamical correlation step. Second, to remove the possible intruder states, a real level shift[36] of 0.3 au was applied. These differences are most probably responsible for the disagreement between ours and Andersson's results. However, since our calculations can be considered simply a refinement over Andersson's, we think that her value of the vibrational frequency is just accidentally better than ours when compared to the experimental frequency,[3] $\Delta G_{1/2}$ = 505 cm^{-1}. On the other side, the experimental bond length[2] of R_e = 1.726 Å compares well with our theoretical value (1.736 Å). We nonetheless think that the VCr molecule deserves further investigations and may certainly be the topic for a future work.

Finally, the calculated ionization potential is 6.03 eV, the electron affinity is 0.88 eV, and the dipole moment is 0.91 D. This latter value is a consequence of a charge transfer of 0.11e from V to Cr.

The ground state of chromium atom is Cr 3d^{5}4s^1 ($^7S_3$) and of vanadium[33] is V 3d^{3}4s^2 ($^4F_{3/2}$). In principle, they would allow to generate at most a triple bond. However, as in the case of tungsten, Cr promotes one electron on the V atom to form an excited 3d^{4}4s^1 state to allow a higher bond multiplicity. The natural orbital occupation for the ground state is the following: $(s\sigma)^{1.90}$ $(d\sigma)^{0.93}$ $(d\pi)^{3.64}$ $(d\delta)^{3.28}$ $(s\sigma^*)^{0.10}$ $(d\sigma^*)^{0.07}$ $(d\pi^*)^{0.36}$ $(d\delta^*)^{0.72}$, that corresponds to an EBO of 4.24, hence a weak quintuple bond.

The ground state of the anion VCr$^-$ is a triplet $^3\Delta$ with one unpaired electron located in a dδ orbital and the other one located in an orbital with mixed character of sσ^* and 4p atomic orbital. The dominant electronic configuration is $|\Psi_{^3\Delta}\rangle = 0.62|d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1\rangle$ and the spectroscopic constants are as follows: equilibrium bond length, R_e = 1.745 Å, vibrational frequency, $\Delta G_{1/2}$ = 652 cm^{-1}, and dissociation energy, D_e = 2.03 eV (D_0 = 1.99 eV). The singlet state, $^1\Sigma^+$, is calculated at 1536 cm^{-1} above the triplet ground state. Finally, the occupation numbers of the molecular orbitals are $(s\sigma)^{1.99}$ $(d\sigma)^{1.81}$ $(d\pi)^{3.69}(d\delta)^{2.61}$ $(s\sigma^*)^{1.01}$ $(d\sigma^*)^{0.18}$ $(d\pi^*)^{0.31}$ $(d\delta^*)^{0.40}$, and the calculated bond order for the anion is 4.11, which implies the existence of a quintuple bond weakened compared to the neutral VCr.

Excited States. The first five vertical excited states are collected in Table 8. We find that the first transition at 290 cm^{-1} corresponds to the spin–orbit splitting of the $^2\Delta$ ground state. The second transition is a vertical excitation from the doubly occupied dσ orbital to the empty dδ orbitals, and appears at 5814 cm^{-1}, in reasonable agreement with the calculation of Andersson[16] which obtains this transition (minimum-to-minimum) at 4299 cm^{-1}. The following four excited states correspond to the spin–orbit splitting of the A$^4\Delta$ state that presents mixed s$\sigma \rightarrow$ sσ^* and d$\delta \rightarrow$ dδ^* transitions. The calculations of Andersson locate this A$^4\Delta$ state at 8325 cm^{-1}, about 370 cm^{-1} lower than our value. In the resonant two-photon ionization spectroscopy experiment,[2] the authors found a reasonably strong transition to a $^2\Delta_{5/2}$ at 14371 cm^{-1} that fits well with the C $^2\Delta_{5/2}$, computed at 14105 cm^{-1} by us and at 12943 cm^{-1} by Andersson. As it was noted by Morse,[2] of particular interest is also the B$^4\Delta$ state that in our calculation is split into 4 components ranging from 11986 to 13072 cm^{-}1 (11703 in Andersson's work), and that exhibits also a moderately intense oscillator strength (within this set of excitations). This transition was measured at 13160 in the preliminary study by Alex and Leopold.[3]

3.2.2. VMo. The ground state of the neutral VMo is calculated to be a doublet $^2\Delta$ with the following dominant electronic configuration $|\Psi_{^2\Delta}\rangle = 0.65|d\sigma^2 d\pi^4 d\delta^3 s\sigma^2\rangle$, in agreement with the experimental findings,[4] and shows a pronounced multireference character although reduced compared the ground state of VCr. The computed spectroscopic constants are listed

Table 8. Low-Lying Vertical Excited States for Neutral VCr Including Spin-Orbit Coupling[a]

state	SF	configuration	excitation	ΔE_{SF}	ΔE_{SO}	exp[b]	f
5/2	$A^2\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2$		0	0	0	
3/2					290		0
1/2	$A^2\Sigma^+$	$d\sigma^1 d\pi^4 d\delta^4 s\sigma^2$	$d\sigma \rightarrow d\delta$	5674	5814	4485	0
1/2	$A^4\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$ +	$d\delta \rightarrow d\delta^*$ +	8670	8702	9220	0
		$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$			0	
3/2					8752		0
5/2					8824		0
7/2					8895		0
5/2	$B^2\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$ +	$d\delta \rightarrow d\delta^*$ +	10497	12502	12160	0
		$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$				0
3/2					12615		0
3/2	$A^2\Pi$	$d\sigma^2 d\pi^3 d\delta^4 s\sigma^2$	$d\pi \rightarrow d\delta$	10897	12306		0
1/2					13390		0
7/2	$B^4\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$ +	$d\delta \rightarrow d\delta^*$ +	11076	11986	13160	0.00012
		$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$				
5/2					12589		0.000098
1/2					12795		0.00017
3/2					13072		0.00014
3/2	$C^2\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$ +	$d\delta \rightarrow d\delta^*$ +	12972	13251		0
		$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$				
5/2					14105	14371[c]	0.00074
5/2	$D^2\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$ +	$d\delta \rightarrow d\delta^*$	13027	13138		0
		$d\sigma^1 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\sigma \rightarrow s\sigma^*$				
3/2					13207		0.00011
13/2	A^2I	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	15981	15984		0.00018
11/2					16258		0
7/2	$A^2\Phi$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	19612	19723		0
5/2					19809		0.0014

[a] The main spin-free contributions are given in the second column. Relative energies (ΔE_{SF}) and (ΔE_{SO}) are in cm^{-1}. f is the oscillator strength. For simplicity, this table includes all the states between 0 and 10000 cm^{-1} and only the spin allowed excited states in the range 10000−25000 cm^{-1}. The states are labelled according to the complete list of excitation energies given in the Supporting Information. [b] Ref 3 preliminary results, with assignment from the present work. [c] Ref 2.

Table 9. Spectroscopic Constants for VMo and VMo$^-$ Computed at the CASSCF/CASPT2 Level of Theory[a]

	R_e	$\Delta G_{1/2}$	D_e	D_0	D'_e	IP	EA	μ
VMo	1.897	514	3.65	3.60	3.45	6.88	0.78	0.07
exp.	1.8766[b]	503[c]					0.93[c]	
VMo$^-$	1.845	604	4.33	4.29		0.78		
exp.		576[c]						

[a] Bond lengths are given in Å; vibrational frequencies in cm^{-1}; energies in eV. D_e and D_0 are obtained following the dissociation channel along the PES. D'_e is calculated using the isolated atoms in their ground states. Dipole moment (μ) in Debye. [b] Ref 4. [c] Ref 5 preliminary results for $^{51}V^{92}Mo$.

in Table 9 together with the available experimental results. The theoretical equilibrium bond length, R_e = 1.897 Å, compares well with the experimental value, R_e = 1.8766 Å.[4] The vibrational frequency, $\Delta G_{1/2}$ = 514 cm^{-1}, is just slightly overestimated with respect to the experimental value,[5] $\Delta G_{1/2}$ = 503 cm^{-1}.

The PES computed at the CASSCF level exhibits the presence of a flat second minimum at about 2.2 Å, but this feature disappears when the dynamic correlation is included in the CASPT2 step. The calculated dissociation energy from the potential surface is D_e = 3.65 eV (D_0 = 3.60 eV), and the value obtained from the isolated atoms in their ground state is D'_e = 3.45 eV, different from D_e since the dissociation channel does not lead to the ground state of the vanadium atom. The calculated ionization potential and electron affinity are 6.88 and 0.78 eV, respectively. The latter value is not far from the experimental electron affinity of 0.93 eV. Finally, the dipole moment, μ = 0.07 D, is notably lower than that for the rest of the dimers, with a small charge transfer of 0.08e from Mo to V. The ground state of the isolated atoms is Mo $4d^5 5s^1 (^7S_3)$ and V $3d^3 4s^2 (^4F_{3/2})$ and eventually only a triple bond might be formed from these electronic configurations. The calculated occupations for the orbitals are $(s\sigma)^{1.92}$ $(d\sigma)^{1.85}$ $(d\pi)^{3.75}$ $(d\delta)^{2.65}$ $(s\sigma^*)^{0.08}$ $(d\sigma^*)^{0.15}$ $(d\pi^*)^{0.25}$ $(d\delta^*)^{0.36}$, which generates an EBO of 4.66 (i.e., a quintuple bond), suggesting the promotion of one electron from the 4s of the vanadium atom to an excited state of $3d^4 4s^1$ type.

The ground state for the molecular anion, VMo$^-$, is found to be a singlet $^1\Delta$, with the following dominant configuration: $|\Psi_{^1\Delta}\rangle = 0.57|d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1\rangle$. The calculated spectroscopic constants are the following: equilibrium bond length R_e = 1.845 Å, vibrational frequency $\Delta G_{1/2}$ = 604 cm^{-1}, and dissociation energy D_e = 4.33 eV (D_0 = 4.29 eV). The comparison with the available experimental results for $\Delta G_{1/2}$ is satisfactory

Table 10. Low-Lying Vertical Excited States for Neutral VMo Including Spin-Orbit Coupling[a]

state	SF levels	configuration	excitation	ΔE_{SF}	ΔE_{SO}	f
5/2	$A^2\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2$			0	
3/2					673	0
1/2	$A^2\Sigma^+$	$d\sigma^1 d\pi^4 d\delta^4 s\sigma^2$	$d\sigma \rightarrow d\delta$	4911	5174	0
3/2	$A^4\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$ + $d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$s\sigma \rightarrow s\sigma^*$ + $d\delta \rightarrow d\delta^*$	9885	9937	0
1/2					9980	0
5/2					10089	0
7/2					10320	0
3/2	$B^2\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	11188	11472	0.000027
5/2					11583	0.00023
3/2	$A^2\Pi$	$d\sigma^2 d\pi^3 d\delta^4 s\sigma^2$	$d\pi \rightarrow d\delta$	11956	11991	0.0012
1/2					12552	0.000016
3/2	$C^2\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^*$	14144	14408	0.000016
5/2					14508	0.00053
3/2	$D^4\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^1 (d\delta^*)^1 (s\sigma^*)^1$	$d\delta \rightarrow d\delta^*$ + $s\sigma \rightarrow s\sigma^*$	23148	23378	0
1/2	30%$D^4\Delta$ + 27%$F^2\Sigma^+$				23425	0
5/2					23591	0.022
7/2					23749	0
1/2	29% $F^2\Sigma^+$ + 28% $D^4\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^1 (d\delta^*)^1 (s\sigma^*)^1$	$d\delta \rightarrow d\delta^*$ + $s\sigma \rightarrow s\sigma^*$	23004	23425	0.016

[a] The main spin-free contributions are given in the second column. Relative energies (ΔE_{SF}) and (ΔE_{SO}) are in cm^{-1}. f is the oscillator strength. For simplicity, this table includes all the states between 0 and 10000 cm^{-1} and only the spin allowed excited states in the range 10000−25000 cm^{-1}. The states are labelled according to the complete list of excitation energies given in the Supporting Information.

(see Table 9). The natural orbital occupation is $(s\sigma)^{1.99}$ $(d\sigma)^{1.87}$ $(d\pi)^{3.78}(d\delta)^{2.72}$ $(s\sigma^*)^{1.01}$ $(d\sigma^*)^{0.12}$ $(d\pi^*)^{0.22}$ $(d\delta^*)^{0.23}$, and the EBO is 4.34, lower than the neutral molecule, despite that its dissociation energy is higher.

Excited States. The lowest vertical excited states of neutral VMo are displayed in Table 10. The first excited state is close in energy to the ground state (673 cm^{-1}) and corresponds to the spin−orbit splitting of the $^2\Delta$ ground state. The second state is an excitation from the $d\sigma$ to a $d\delta$ orbital and is located 5174 cm^{-1} above the ground state. Higher in energy, above 10000 cm^{-1}, we find several excited states with mixed character of $s\sigma \rightarrow s\sigma^*$ and $d\delta \rightarrow d\delta^*$ transitions. There are two regions that are interesting from an experimental standpoint as they exhibit excited states with an intense oscillator strength: the 11000−15000 cm^{-1} and 23000−24000 cm^{-1} regions. In the first interval, there are three states that could be resolved experimentally by R2PI, a $B^2\Delta_{3/2}$ at 11472 cm^{-1}, a $B^2\Delta_{5/2}$ at 11583 cm^{-1}, and a $C^2\Delta_{5/2}$ at 14508 cm^{-1}. In the second interval there are two excited states with an even higher intensity, a $D^4\Delta_{5/2}$ at 23591 cm^{-1} that involves a $d\delta \rightarrow d\delta^*$ transition, and a $F^2\Sigma_{1/2}{}^+$ at 23425 cm^{-1}.

3.2.3. VW. The ground state of neutral VW is a doublet $^2\Delta$, with the following dominant electronic configuration: $|\Psi_{^2\Delta}\rangle = 0.67|d\sigma^2 d\pi^4 d\delta^3 s\sigma^2\rangle$. This ground state also possesses a clear multiconfigurational nature, as the rest of the dimers studied. The theoretical PES shows a small shoulder at longer distances, at CASSCF level, which disappears at the CASPT2 level. The calculated spectroscopic constants (see Table 11) are as follows: equilibrium bond length R_e = 1.936 Å, vibrational frequency $\Delta G_{1/2}$ = 476 cm^{-1}, and spin-free dissociation energy D_e = 4.28 eV (D_0 = 4.25 eV). The D'_e calculated using the isolated atoms in their ground state and including spin−orbit coupling is 3.66 eV. The ionization potential is 7.00 eV, the electron affinity is 0.63 eV, and the dipole moment is μ = 1.71 D. The latter is a consequence of a large charge transfer of 0.18e from W to V. To our knowledge, no experimental results are available for this molecule.

Table 11. Spectroscopic Constants for VW and VW$^-$ Computed at the CASSCF/CASPT2 Level of Theory[a]

	R_e[b]	$\Delta G_{1/2}$[b]	D_e[b]	D_0[b]	D'_e[c]	IP[c]	EA[c]	μ[b]
VW	1.936	476	4.28	4.25	3.66	7.00	0.63	1.71
VW$^-$	1.962	438	4.73	4.70		0.63		

[a] Bond lengths are given in Å; vibrational frequencies in cm^{-1}; energies in eV. D_e and D_0 are obtained following the dissociation channel along the PES. D'_e is calculated using the isolated atoms in their ground states. Dipole moment (μ) in Debye. [b] Spin-free. [c] Spin−orbit.

As we previously discussed, to be able to generate a quintuple bond, the interaction between V and W atoms allows the promotion of one electron within the vanadium atom from its ground state, $3d^3 4s^2 (^4F_{3/2})$, to an excited $3d^4 4s^1$ state, and also from the doubly occupied 6s orbitals of the W atom to one of the empty 5d orbitals. The natural orbital occupation is $(s\sigma)^{1.93}$ $(d\sigma)^{1.85}$ $(d\pi)^{3.76}$ $(d\delta)^{2.66}$ $(s\sigma^*)^{0.07}$ $(d\sigma^*)^{0.15}$ $(d\pi^*)^{0.24}$ $(d\delta^*)^{0.35}$, providing an EBO of 4.70, with a bond multiplicity of five.

The anion, VW$^-$, possesses a triplet $^3\Delta$ ground state that is represented by the following electronic configuration: $|\Psi_{^3\Delta}\rangle = 0.70|d\sigma^2 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1\rangle$ where the extra electron is not paired

Table 12. Low-Lying Vertical Excited States for Neutral VW Including Spin-Orbit Coupling[a]

state	spin-free levels	configuration	excitation	ΔE_{SF}	ΔE_{SO}	f
5/2	$A^2\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^2$		0	0	0
3/2					2146	0
1/2	$34\%A^4\Sigma^+ +$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	8415	7626	0
	$32\%B^2\Sigma^+ +$			8555		
	$24\%A^2\Sigma^+ +$			7716		
	$11\%C^2\Sigma^+$			9058		
3/2	$A^4\Sigma^+$				9465	0
1/2	$60\%B^2\Sigma^+ +$				8926	0
	$30\%A^4\Sigma^+$					
1/2	$62\%C^2\Sigma^+ +$				10044	0
	$31\%A^4\Sigma^+$					
1/2	$58\%A^2\Sigma^+ +$				11795	0
	$40\%C^2\Sigma^+$					
9/2	$A^2\Gamma$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	8807	9732	0
7/2					9928	0
3/2	$A^4\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1 +$	$s\sigma \rightarrow s\sigma^* +$	9785	9180	0
		$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$			0
5/2					10357	0
1/2					10785	0
7/2					10986	0
5/2	$A^2\Delta$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	10582	12502	0.00035
3/2					12614	0.00033
5/2	$B^4\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1 +$	$s\sigma \rightarrow s\sigma^*$	11088	11589	0.00031
		$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$		11644	0
7/2					11644	0
3/2					12072	0.00015
1/2					13390	0
3/2	$A^2\Pi$	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (s\sigma^*)^1$	$d\delta \rightarrow s\sigma^*$	11766	12306	0.00048
1/2					14280	0
5/2	$C^2\Delta$	$d\sigma^1 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\sigma \rightarrow s\sigma^*$	12280	13251	0.0025
3/2					14106	0
11/2	A^2H	$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$	14496	15449	0.00012
9/2					16049	0.00014
7/2	$A^2\Phi$	$d\sigma^1 d\pi^4 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\sigma \rightarrow s\sigma^*$	14938	15881	0.00104
5/2					16580	0
5/2	$D^4\Delta$	$d\sigma^2 d\pi^4 d\delta^3 s\sigma^1 (s\sigma^*)^1$	$s\sigma \rightarrow s\sigma^* +$	17116	17696	0
		$d\sigma^2 d\pi^4 d\delta^2 s\sigma^2 (d\delta^*)^1$	$d\delta \rightarrow d\delta^*$			
7/2					17949	0
3/2					18992	0.00109
1/2					18993	0
5/2	$A^4\Pi$	$d\sigma^2 d\pi^3 d\delta^3 s\sigma^2 (s\sigma^*)^1$	$d\pi \rightarrow s\sigma^* +$	20057	20449	0.00012
		$d\sigma^2 d\pi^3 d\delta^3 s\sigma^2 (d\delta^*)^1$	$d\pi \rightarrow d\delta^*$			
3/2					21331	0
1/2					21880	0
1/2					22559	0

[a] The main spin-free contributions are given in the second column. Relative energies (ΔE_{SF}) and (ΔE_{SO}) are in cm^{-1}. f is the oscillator strength. For simplicity, this table includes all the states between 0 and 10000 cm^{-1} and only the spin allowed excited states in the range 10000−25000 cm^{-1}. The states are labelled according to the complete list of excitation energies given in the Supporting Information.

in the dδ orbitals but is located in the antibonding sσ*. The singlet $^1\Sigma^+$ state is located only 322 cm^{-1} above the triplet state. The calculated equilibrium bond length is $R_e = 1.962$ Å, the vibrational frequency is $\Delta G_{1/2} = 438$ cm^{-1}, and the spin-free dissociation energy is $D_e = 4.73$ eV ($D_0 = 4.70$ eV). The bond order obtained from the following occupation numbers $(s\sigma)^{1.99}$ $(d\sigma)^{1.85}$ $(d\pi)^{3.76}$ $(d\delta)^{2.67}$ $(s\sigma^*)^{1.01}$ $(d\sigma^*)^{0.15}$ $(d\pi^*)^{0.23}$ $(d\delta^*)^{0.34}$ is 4.28, corresponding to a quintuple bond. Also in this case, the EBO of the anion is smaller than that of the neutral molecule, but its dissociation energy indicates a stronger bond.

Table 13. Spectroscopic Constants and Effective Bond Order for Neutral and Anionic Heterodimers[a]

	state	R_e	$\Delta G_{1/2}$	k	D_e	D'_e	IP	EA	EBO
CrMo	$^1\Sigma^+$	1.859	419	3.44	2.63	2.62	8.06	0.25	4.70
CrW	$^1\Sigma^+$	1.919	348	2.89	3.19	2.73	6.75	0.42	4.37
MoW	$^1\Sigma^+$	1.992	414	6.19	5.41	4.92	7.52	0.58	5.17
VCr	$^2\Delta$	1.736	680	7.00	2.19	1.78	6.03	0.88	4.24
VMo	$^2\Delta$	1.897	514	5.11	3.65	3.45	6.88	0.78	4.66
VW	$^2\Delta$	1.936	476	5.32	4.28	3.66	7.00	0.63	4.70
CrMo$^-$	$^2\Sigma^+$	1.866	402	3.16	2.66		0.25		4.35
CrW$^-$	$^2\Sigma^+$	1.965	287	1.96	2.90		0.42		4.11
MoW$^-$	$^2\Sigma^+$	2.012	390	5.50	5.23		0.58		4.72
VCr$^-$	$^3\Delta$	1.745	652	6.44	2.03		0.88		4.11
VMo$^-$	$^1\Delta$	1.845	604	7.05	4.33		0.78		4.34
VW$^-$	$^3\Delta$	1.962	438	4.51	4.73		0.63		4.28

[a] Equilibrium bond lengths (R_e) in Å, vibrational frequencies ($\Delta G_{1/2}$) in cm^{-1}, dissociation energies (D_e, D'_e), ionization potentials (IP) and electron affinities (EA) in eV. The force constant k (mdyn/Å) is computed using the fundamental vibrational frequencies.

Table 14. Calculated Vibrational Frequencies of Each Dimer Computed at the CASPT2 Level of Theory

	$\Delta G_{v+1/2}$					
v	CrMo	CrW	MoW	VCr	VMo	VW
1	419	348	414	680	514	476
2	392	343	412	687	516	471
3	365	336	408	622	515	472
4	336	328	405	488	493	467
5	310	319	400	405	408	463
6	287	310	395	318	332	458
7	270	300	389	243	347	452
8	260	291	383	187	306	446
9	255	283	376	167	311	439

Excited States. We have computed the first vertical excited states for neutral VW (See Table 12). The first excited state is located at 2146 cm^{-1}. This transition corresponds to the spin–orbit splitting of the $^2\Delta$ ground state. In the range 12000–16000 cm^{-1} there are several excited states with a reasonably intense character and may be used for experimental purposes.

4. DISCUSSION AND CONCLUSIONS

Group VI heterodimers (CrMo, CrW and MoW) have 12 valence electrons which, in the ground state, are paired in six bonding orbitals composed of the nd and $(n+1)$s atomic orbitals, and give rise to a $^1\Sigma^+$ electronic state; the heterodimers with vanadium (VCr, VMo, and VW) have one unpaired electron, located in one of the bonding dδ orbitals, that form a $^2\Delta$ ground state. All six dimers show a pronounced multireference nature of the ground state, whose dominant electronic configuration has a total weight of no more than 0.67 (MoW) that precludes the use of single-reference based methods and, therefore, multiconfigurational methods as CASSCF/CASPT2 are mandatory for the study of these systems. The PESs reveal that, at the CASPT2 level, all dimers show a deep minimum at short bond distances, but only VCr shows a shelf-like potential at longer distances. Inspection of the spectroscopic constants (see Table 13) shows that for both the group VI heterodimers and for the mixed vanadium–group VI ones, the equilibrium bond length increases when descending in the group, because of the bigger atomic size of the heavier metals. The dissociation energies, both along the dissociation channel and relative to the isolated atoms in their ground state, increase along the series, a fact that has as a consequence the increase of bond multiplicity and of the EBO. An exception on the trend is found for CrW that exhibits a bond order of 4.37, lower than the one corresponding to CrMo, 4.70. In vanadium complexes a similar trend is clearly observed. From these values we can say that all dimers can be described having a quintuple bond, except MoW which exhibits a sextuple bond. This latter value corresponds to the highest bond order attained among heterodimers.

One peculiarity of the EBO is that, when we compare its value for the neutral dimer with that of the corresponding anion, the trend of the dissociation energy in some cases is not followed. However, if we simply look at the force constants, the EBO trend is followed, with the only exception being the VMo dimer. This irregular behavior between force constants and dissociation energy is likely because they cannot be related with a simple harmonic approximation.

In the case of the anions, the ground state for the group VI heterodimers (CrMo$^-$, CrW$^-$, and MoW$^-$) is always a $^2\Sigma^+$, with one unpaired electron in the antibonding sσ^* orbital. In the case of the vanadium heterodimers, the ground state changes according to the atom attached to V: a $^3\Delta$ for VCr$^-$, a $^1\Delta$ for VMo$^-$, and a $^3\Delta$ for VW$^-$. As a further help for future experimental investigations, we have also computed the first nine vibrational levels of each dimer (Table 14).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Further details are given in four tables on low-lying vertical excited states for VCr, VMo, and VW. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: iinfant76@gmail.com.

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