Electronic Structure of Bis(2,4-pentanedionato-*O,O′*)oxovanadium(IV). A Photoelectron Spectroscopy, Electronic Spectroscopy, and ab Initio Molecular Orbital Study

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The electronic structure of the title $VO(acac)_2$ complex has been investigated using effective core potential configuration interaction ab initio calculations, UV−photoelectron spectroscopy, and electronic spectroscopy. The metal−ligand bonding with the equatorial $acac^-$ ligands is dominated by σ interactions involving the filled ligand orbitals and the empty orbitals of the d^1 vanadium(IV) ion. The oxovanadium interactions involve a larger metal-d participation thus resulting in a strong V−O bonding having partial triple-bond character. Additional three-orbital−four-electron stabilizing interactions involving the filled $acac^-$ MOs and the oxovanadium orbitals further reinforce both the axial and equatorial bonds. The unpaired metal-d electron is completely localized in the nonbonding $d_{x^2-y^2}$ orbital. The low ionization energy of the photoelectron spectrum has been fully assigned on the basis of combined ΔSCF and configuration interaction calculations. The same theoretical approach has, in addition, provided a good fitting of frequencies associated with “d−d” and charge transfer electronic transitions.

Introduction

The oxovanadium(IV) ion (VO^{2+}) plays a dominant role in the vanadium(IV) chemistry.[1] Among its complexes, the vanadyl acetylacetonate ($VO(acac)_2$) is certainly the most representative species. $VO(acac)_2$ has been the subject of many experimental investigations devoted to its interesting paramagnetic[2−4] and physicochemical[1,5,6] properties, mainly associated with the $3d^1$ electronic configuration.

$VO(acac)_2$ possesses a square-pyramidal arrangement of the five coordinated oxygen atoms, with the vanadium atom close to the center of gravity of the pyramid. Early X-ray crystal structure determinations[7] and a more recent gas-phase electron diffraction study[8] have pointed to a monomeric structure of C_{2v} symmetry, with the V=O bond along the 2-fold axis. Magnetic susceptibility and ESR data have indicated a magnetic moment and paramagnetic resonance factors both consistent with a single unpaired electron.[1−3] In spite of these experimental efforts, less attention has been paid to theoretical aspects associated with the $VO(acac)_2$ molecule, since only ligand-field[9] and semiempirical calculations[10,11] have appeared in the literature.

In this context, we embarked on a combined study involving ab initio calculations, UV−photoelectron (PE) spectroscopy,[12] and electronic spectroscopy to investigate the electronic structure of $VO(acac)_2$. The very good resolution of its PE spectra offers, in addition, the possibility to probe theoretical results by a direct one-to-one comparison of experimental ionization energies (IEs) with calculated data.

Experimental Section

$VO(acac)_2$ (Aldrich) was purified by sublimation in vacuo. He I and He II PE spectra were measured as described elsewhere.[12] Resolution measured on the He $1s^{-1}$ line was around 25 meV. The PE spectra were recorded in the 160−180 °C temperature range. The spectra were deconvoluted by fitting the spectral profiles with a series of asymmetrical Gaussian curves after subtraction of the background.[13] The area bands thus evaluated can be affected by errors smaller than 5%. Optical absorption UV−vis spectra were recorded with a Beckman DU 650 spectrophotometer.

Theoretical Methods

Ab initio effective core potential (ECP) were employed in the molecular calculations using the restricted Hartree−Fock (RHF) method for the closed-shell states, and the restricted open Hartree−Fock (ROHF) method for the open-shell states. The ionization energies of the lower lying ionic states of each symmetry were evaluated using ΔSCF procedures, which account only for relaxation contribution to the total reorganization energy. The effect of electron correlation was considered by using the configuration interaction (CI) procedure including all-single and double-excitations (CISD) from the single HF reference. Since a complete CISD treatment would generate an enormous number of configuration state functions (CSFs), the treatment was limited to using the highest 10 occupied MOs and the lowest 10 virtual orbitals having dominant metal 3d, 4s, 4p and ligand π_4 character (10/10 expansion, ∼40 000 CSFs generated). In addition, the ionization energies of the two most stable states of the cation ($^3B_2$ and $^1A_1$) were also calculated by a more extended CISD 18/10 expansion (∼430 000 CSFs generated). Because of the variational collapse, the ΔSCF procedure allows the calculation of the ionization energy only for the lowest-lying state of each symmetry. Therefore, for those states only CI calculations with the appropriate SCF orbitals were performed. The IEs of the higher-lying ionic states were evaluated using, as reference, the SCF orbitals of the lowest state of each symmetry, by solving the

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Table 1. Ab Initio Eigenvalues and Mulliken Population Analysis of the Outermost $VO(acac)_2$ MOs

MO	energy, eV		population, %							character
			V							
	$-\epsilon$ [a]	ΔSCF	3d	4s	4p	O	4O	$2(C_3H)$	$4(CH_3)$	
$14a_1$	15.41 (15.76)	9.92	98	0	0	0	2	0	0	$d_{x^2-y^2}$
$12b_2$	9.15 (9.55)	8.58[b]	0	0	0	3	29	66	2	π_3
$13a_1$	9.41 (9.85)	8.83[b]	1	0	0	1	25	71	2	π_3
$10b_1$	11.50 (12.05)	10.60[b]	0	0	0	5	59	18	18	n_-
$9a_2$	12.07 (12.63)	11.22[b]	4	0	0	0	55	23	18	n_-, d_{xy}
$9b_1$	12.35 (12.79)		13	0	0	60	18	5	4	π (V−O), d_{yz}
$11b_2$	12.54 (13.03)		8	0	0	56	20	10	6	π (V−O), d_{xz}
$10b_2$	12.96 (13.58)		7	0	0	11	52	15	15	n_+, d_{xz}
$12a_1$	13.20 (13.71)		6	4	0	35	35	9	11	σ (V−O), n_+, d_{z^2}
$11a_1$	13.78 (14.37)		16	0	0	31	30	13	10	n_+, σ (V−O), d_{z^2}
$8a_2$	13.87 (14.77)		0	0	0	0	64	11	25	π_2
$8b_1$	14.52 (15.42)		7	0	0	13	43	6	31	π_2, d_{yz}

	atomic charge (eu)
V ($4s^{0.39}$, $4p^{0.05}$, $3d^{2.87}$) ($d_{x^2-y^2}{}^{1.07}$, $d_{z^2}{}^{0.49}$, $d_{xy}{}^{0.36}$, $d_{xz}{}^{0.50}$, $d_{yz}{}^{0.45}$)	+1.69
O	−0.48
2(acac)	−1.21

[a] Eigenvalues in parentheses refer to $VO(acac')_2$ data. [b] ΔSCF energy of the triplet state.

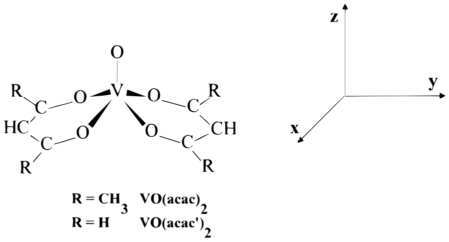

Figure 1. Geometry of the $VO(acac)_2$ complex.

secular CI matrix for the second electronic state. This procedure allows a semiquantitative evaluation of the reorganization energy upon ionization.[14]

The model $VO(acac')_2$, where the methyl groups of the acac rings were replaced by hydrogen atoms, was used for CI calculations to enhance computational efficiency. There is, in fact, evidence that depletion of the methyl groups does not alter the nature and the energy sequence of the outermost MOs but simply results in an almost constant (~0.5 eV) upward energy shift (Table 1). Thus, estimated CI IEs for $VO(acac)_2$ were obtained from CI IEs for the model $VO(acac')_2$ reduced by the mentioned energy shift.

Excitation energies were evaluated by the total energy difference between the $^2A_1$ ground state and various excited doublet states using combined ΔSCF and CISD (10/10) procedures.

The ECPs of Hay *et al.*,[15] which explicitly treat the valence orbitals, and the basis set contracted as [2s,2p,2d] were used for the vanadium atom. For C and O atoms the ECPs and double-ζ basis sets of Stevens *et al.* were used,[16] while the standard 31G basis was adopted for H atoms.[17] For all the calculations, the gas-phase electron diffraction C_{2v} structure[8] was adopted (Figure 1).

All the calculations were performed by using the HONDO-8 program[18] on IBM ES/9000 and Cray C92 systems.

Results and Discussion

Theoretical Data. The nature of frontier molecular orbitals of the planar acetylacetonate anion ligand ($acac^-$) has been thoroughly discussed.[12,19] They consist of the five out-of-plane π orbitals ($\pi_1-\pi_5$) characteristics of a five-center−six-electron p_z orbital system and of the symmetry combinations of the two in-plane lone pair (n_+ and n_-) of the carbonyl oxygens. Previous studies on several metal acac complexes have indicated[12,19] that the in- and out-of-phase combinations of the π_{2-3} and the $n_\pm$ MOs are well suited for the metal−ligand bonding.

The metal−ligand interactions can be better understood in terms of interactions between the vanadyl group and equatorial ligands since previous data of a large variety of complexes containing VO^{2+} have indicated that the identity of the VO unit remains ubiquitous in vanadyl chemistry.[1,10]

Eigenvalues and population analysis of the outermost filled MOs of the $^2A_1$ ground state of $VO(acac)_2$ are compiled in Table 1. On the basis of the dominant MO character, they can be grouped in three categories: (i) the metal-based MO responsible for the d^1 configuration; (ii) the symmetric and antisymmetric combinations (a and b, respectively, in the C_{2v} point group) of the mentioned filled $acac^-$ ligand orbitals admixed, in some cases, with metal 3d orbitals, and (iii) the MOs representing the axial V−O interactions.

The $14a_1$ MO represents the unpaired metal-d electron and is completely localized in the nonbonding $d_{x^2-y^2}$ orbital. This agrees well with solution EPR spectra which indicate *g* values very close to the free electron value.[2] Note that this partially filled orbital does not represent the HOMO but lies considerably more stable than many double occupied ligand orbitals.[20] This aspect, however, has been addressed theoretically[21] and repre-

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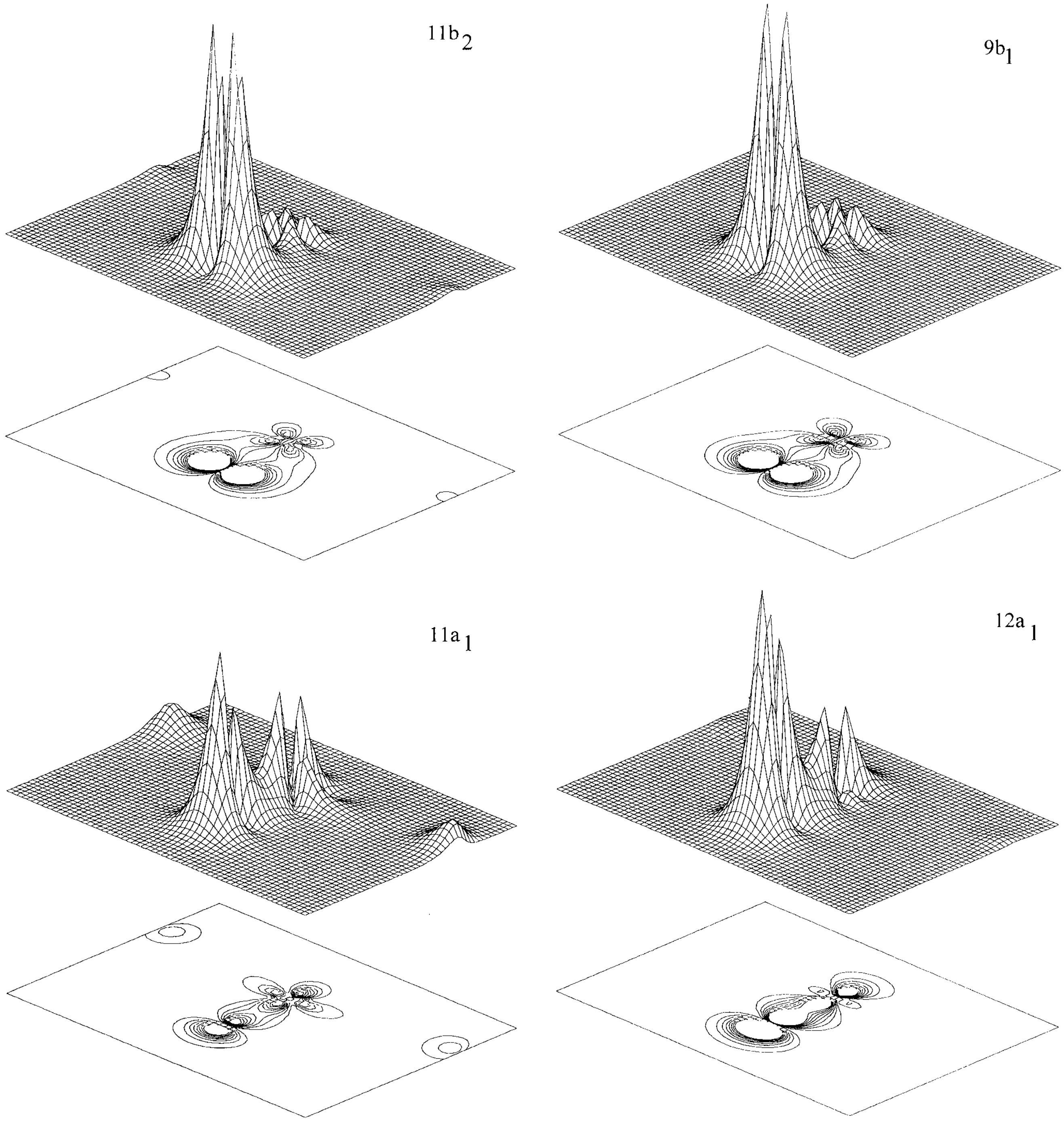

Figure 2. Electron density contour plots of $11a_1$, $12a_1$, and $11b_2$ MOs in the *yz* plane and $9b_1$ MO in the *xz* plane. The first contour is 0.05 e·au^3 and the interval between successive contours is 0.006 e·au^3.

sents a common feature of SCF calculations of many transition metal complexes possessing partially filled metal-d orbitals.[22]

The σ and π V−O interactions are contained into the $11a_1$, $12a_1$ and into the $11b_2$, $9b_1$ MOs, respectively, and involve a large metal-d participation (Figure 2). In particular, the σ bonding involves the O_{2p} AOs and the metal d_{z^2} orbital, while the π bonds involve the d_{xz} and d_{yz} orbitals. The calculated V−O bond index (2.11) is consistent with a formal V═O double bond description, with a partial triple-bond character. This data accord well with the very short experimental[7,8] and calculated[23] V−O distance (1.56 Å) and the strong experimental (997 cm^{-1})[24] and calculated (1215 cm^{-1})[23] V═O stretching, as well as with previous multiple-scattering Xα calculations[25] of simpler oxovanadium(IV) species.

The bonding interactions with the equatorial acac$^-$ ligands involve the donation of carbonyl lone pairs into the metal d_{xy} orbital which, by symmetry, does not participate in the V−O bonding. There are indications of additional VO−acac interactions into the $9b_1$, $11b_2$, $10b_2$, $12a_1$, $11a_1$, and $8b_1$ MOs. These additional interactions are better considered in terms of three-orbital−four-electron interactions involving the filled acac$^-$ MOs and O_{2p} lone pairs, and the empty V(IV) 3d orbitals with a net bonding contribution for both the axial and equatorial

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Table 2. Comparison of Calculated and Experimental Optical Absorption Frequencies (cm^{-1}) for $VO(acac)_2$

transition	ΔSCF	CISD 10/10	experimental[a]	comments
$^2B_2 \leftarrow {}^2A_1$	14 724	15 366	14 200	$d_{x^2-y^2} \rightarrow d_{xz}$
$^2B_1 \leftarrow {}^2A_1$	15 136	15 333		$d_{x^2-y^2} \rightarrow d_{yz}$
$^2A_2 \leftarrow {}^2A_1$	17 326	17 212	16 950	$d_{x^2-y^2} \rightarrow d_{xy}$
$^2A_1 \leftarrow {}^2A_1$	25 250	25 372	25 400	$d_{x^2-y^2} \rightarrow d_{z^2}$
$^2B_1 \leftarrow {}^2A_1$	17 702	32 684	33 400	π (V−O) → $d_{x^2-y^2}$
$^2B_2 \leftarrow {}^2A_1$	17 796	32 964		π (V−O) → $d_{x^2-y^2}$
$^2A_1 \leftarrow {}^2A_1$	18 210	34 930		π (V−O) → d_{xz}
$^2A_1 \leftarrow {}^2A_1$	18 366	35 354		π (V−O) → d_{yz}
$^2A_2 \leftarrow {}^2A_1$	18 504	40 811	37 320	π (V−O) → d_{yz}
$^2A_2 \leftarrow {}^2A_1$	18 711	40 590		π (V−O) → d_{xz}
$^2A_2 \leftarrow {}^2A_1$	47 024			$\pi_3 \rightarrow \pi_4$
$^2B_2 \leftarrow {}^2A_1$	50 127			$\pi_3 \rightarrow d_{x^2-y^2}$
$^2A_2 \leftarrow {}^2A_1$	58 333	66 612		$n_- \rightarrow d_{x^2-y^2}$
$^2A_1 \leftarrow {}^2A_1$	120 700			$n_- \rightarrow \pi_4$

[a] Experimental values have been obtained in CH_3CN solution (Figure 3).

bonds. This is in agreement with the larger V−O(acac) bond dissociation energy,[26] and the stronger V−O(acac) IR stretching,[24] compared to other $M(acac)_2$ complexes.[23,24,27,28] This overall bonding picture can be contrasted with that of d^8 metal bis(acac) complexes[12] in which the net metal−ligand stabilization essentially involves filled $acac^-$ MOs and the empty nd_{xy} and $n + 1$s metal orbitals. The atomic charge presently found over the $(acac)_2$ ligand (−1.21 eu) indicates a ligand-to-metal charge donation of 0.79 eu from filled MOs of the $(acac)_2{}^{2-}$ cluster to the empty 3d and 4s metal orbitals (Table 1). The greater donation (−0.36 eu) is allocated into the $3d_{xy}$ subshell. The complementary −0.42 eu is distributed into the d_{z^2} and $d_{xz,yz}$ orbitals.

In this context, the relative energy ordering of virtual 3d-based MOs becomes a sensitive tool to test the magnitude of metal−ligand interactions. The relative energy ordering of virtual 3d-based orbitals in vanadyl complexes has been the object of a great debate[5,9,29,30] since the classical paper of Ballhausen and Gray.[10] In fact, controversial assignments of "d−d" optical absorption spectra of vanadyl complexes have been proposed.[5,9,29,30] Present experimental and calculated excitation energies related to "d−d" transitions of $VO(acac)_2$ are compared in Table 2. The strong metal−ligand admixture ($11a_1$ and $12a_1$ MOs) involving both the axial V−O and the equatorial V−O (acac) σ-bonds, is responsible for the topmost energy position of the d_{z^2} (a_1) MO, while a selective acac→M charge-transfer involving the internal π_2 ($8b_1$) acac MO, is responsible for the energy splitting of the $d_{xz}(b_2)$ and $d_{yz}(b_1)$ orbitals which, in the axial field approximation of the VO^{2+}, ion are degenerate (π_u, $C_{\infty v}$). The present results agree with both the early energy orbital sequence proposed for the $VO(H_2O)_5{}^{2+}$ ion,[10] as well as with the proposed assignment[5] of $VO(acac)_2$ "d−d" optical spectra. Moreover, the present calculated CISD transition energies almost reproduce the experimental values taken in solution (Table 2).

Several charge-transfer (CT) and ligand-to-ligand electronic excitations have also been evaluated (Table 2). Among them, the lowest calculated energy transitions (∼32 800 cm^{-1}) are those associated with the promotion of one electron from MOs formally representing the π (V−O) interactions to the partially filled $d_{x^2-y^2}$ metal-based MO ($9b_1 \rightarrow 14a_1$ and $11b_2 \rightarrow 14a_1$ transitions). The next four excited states are due to the excitation of one electron from the two MOs formally representing the π V−O interactions ($9b_1$ and $11b_2$ MOs) to the metal based d_{xz} and d_{yz} empty orbitals (∼35 200 and ∼40 700 cm^{-1}).

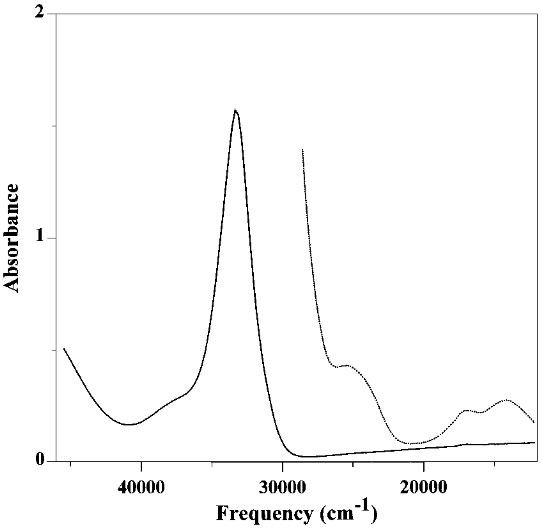

Figure 3. Optical absorption spectrum of $VO(acac)_2$ in acetonitrile solution 3.0×10^{-5} M (solid line) and 5.0×10^{-3} M (dashed line).

The electronic absorption spectrum of $VO(acac)_2$ in the region >30 000 cm^{-1} has not been previously reported. The analysis of the optical spectrum of $VO(acac)_2$ in acetonitrile (Figure 3) reveals a high intensity band centered at 33300 cm^{-1} with a shoulder at 37320 cm^{-1}. In accordance with present calculations, these bands can be assigned to the π (V−O) → $d_{x^2-y^2}$ and π (V−O) → d_{xz}, d_{yz} electronic excitations (Table 2). This assignment is in agreement with early results found for the $VO(H_2O)_5{}^{2+}$ ion,[10] which indicated analogous electronic excitations in the near-UV region.

Finally, calculated $\pi_3 \rightarrow \pi_4$, $n_- \rightarrow \pi_4$ intraligand and $\pi_3 \rightarrow$ d, $n_- \rightarrow$ d CT transitions have been found higher in energy (>40 000 cm^{-1}) and therefore observable in the far-UV region. Some representative examples of each class of these excitations are reported in Table 2.

Photoelectron Spectrum. The low IE region (<12.5 eV) of the He I PE spectrum of $VO(acac)_2$ (Figure 4) consists of seven well-resolved bands (**a**−**g**) and of a shoulder **f**′ associated with the band **f**. All these bands have approximately the same relative intensity (Table 3 and Figure 4). Moreover, a low intensity band (**x**) appears at the onset of the spectrum. Under the more energetic He II radiation, the band **x** as well as the bands **e**−**g** clearly increase relative to the remaining spectral features (Table 3 and Figure 4).

The Koopmans sequence inferred from the present ground state calculations (Table 1) lends itself to some criticism since it would predict the orbital energy of the half occupied ($14a_1$) metal-d based MO below several double occupied MOs. This unusual (in classical terms of crystal field theory) pattern of orbital energies does not represent an artifact of different SCF procedure to treat open- and closed-shell orbitals, since also for the majority of transition metal complexes with closed-shell configuration, Koopman's theorem predicts the d^{-1} ionizations considerably more internal than many ligand-based MOs, in contrast with the experimental IE sequences.[12,31] This paradoxical situation is due to the large interelectronic repulsion associated to the small metal d orbitals.[21] Therefore, Koopman's approximation does not provide a safe basis for the interpretation

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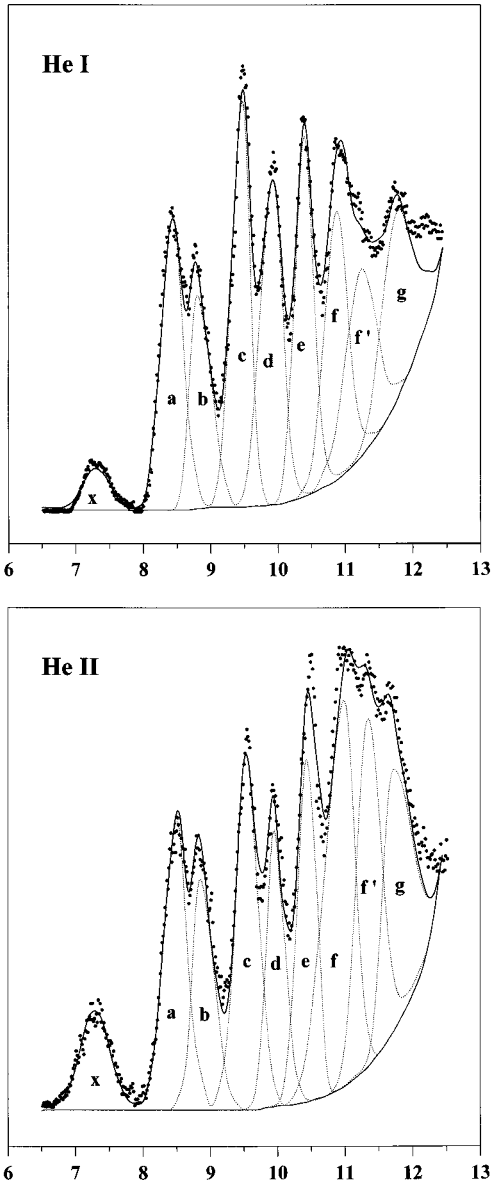

Figure 4. He I and He II PE spectra of $VO(acac)_2$ in the low-IE region: experimental spectrum (dotted line), Gaussian components (dashed line), and convolution of Gaussian components (solid line).

of present PE spectra, and hence, an explicit treatment of relaxation and correlation energies upon ionization is necessary to arrive at the correct PE assignment.[31]

Accordingly, present ΔSCF calculations show that a considerably larger relaxation energy (5.49 eV) is associated with the $(14a_1)^{-1}$ ionization than for ligand-based ionizations (0.73 eV, Table 1). Nevertheless, the $^3B_2$ $(...(13a_1)^2(12b_2)^1(14a_1)^1)$ state still remains the ground state of $VO(acac)_2^+$, but the $^1A_1$ $(...(13a_1)^2(12b_2)^2)$ state is now closer in energy. In view of this large relaxation energy, a large differential electron correlation energy would be expected for metal- and ligand ionized states.[31] Correlation effects have been, therefore, accounted for by performing individual CISD 10/10 calculations for each ion state of the simpler $VO(acac')_2$ model. More extended CISD 18/10 calculations have been, in addition, performed for the $^3B_2$ and $^1A_1$ states in order to better evaluate the differential correlation energy for representative, closer lying ligand and metal-ionized states.

CISD IE values are compiled in Table 3 and compared with ΔSCF data. It becomes evident that, even taking some account of correlation energies (CISD 10/10) the $^3B_2$ state still remains the ground state of the $VO(acac')_2^+$ ion. The further CISD (18/10) extension to the lower-lying $^3B_2$ and $^1A_1$ states results in the $^1A_1$ ground state (Table 3). On the basis of present calculations, the assignment of the lower IE spectral features becomes straightforward. Moreover, note that the CI IE values, once corrected for the shift due to the omission of methyl groups in the model presently adopted (vide infra), provide a very accurate fitting of experimental IE values (Table 3). Thus, the onset band **x** is assigned to the d^{-1} ionization also in accordance with the observed He I vs He II relative intensity variation (Table 3). It is well-known, in fact that the He II cross section (relative to He I) of metal 3d subshells is considerably greater than that associated to O_{2p} and C_{2p} ligand-based MOs.[13,32] A similar low intensity onset feature has been observed in the PE spectra of VCl_4[33] and $V(hfa)_3$[19] and it has been assigned to the d^{-1} ionizations, even though the related IE values are considerably shifted to higher energies. This, however, represents a well-known effect due to the different charge in the metal center.

The following four well-resolved bands **a**−**d** represent ionizations from the π_3 and n_- symmetry combinations. These bands resemble the unsplit (due to a pseudotetrahedral molecular arrangement) π_3 and n_- acac-based bands found in $Zn(acac)_2$,[34] shifted to higher IEs because of the expected larger ligand-to-metal charge donation. These bands do not increase in the He II spectrum in accordance with their almost pure ligand character. Bands **e** and **f** are associated with the ionization of MOs mostly representing π V−O bonds. The pronounced energy splitting ($\Delta IE_{\mathbf{e-f}} = 0.55$ eV) is evidence of differential perturbations due to equatorial ligands. Finally, the **f**′ and **g** features represent the $(10b_2)^{-1}$ (n_+) and $(12a_1)^{-1}$ (σ V−O) ionizations. Note that the IE differences associated with the production of singlet and triplet final states (Table 3) are negligible. This observation agrees well with the sharpness of various bands (Figure 4). Finally, it should be pointed out that the assignment of bands **e**−**g** is correctly tuned with their relative intensity enhancement in the He II spectrum. This is due to the greater (relative to C_{2p}) cross section of 3d subshells under the He II radiation[13,32] and hence to the greater 3d contribution in the corresponding MOs.

This assignment is in general agreement with those of some related bis(acetylacetonate) $Be(acac)_2$, $UO_2(acac)_2$, $Pd(acac)_2$, and $Zn(acac)_2$, complexes.[12,19,31b,34−36] In fact, the IEs of the π_3 and n_- MOs are almost constant (8.5−9 eV and 9.5−10 eV respectively) along the series (Figure 5), thus indicating similar metal−ligand interactions. Note, however, that in the (d^8) $Pd(acac)_2$ complex the more external π_3 ionization is shifted to

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[31] See, for example: (a) Ciliberto, E.; Di Bella, S.; Fragalà, I.; Burton, N. A.; Hillier, I. H.; Kendrick, J.; Guest, M. F. *J. Chem. Soc., Dalton Trans.* **1990**, 849. (b) Burton, N. A.; Hillier, I. H.; Guest, M. F.; Kendrick, J. *Chem. Phys. Lett.* **1989**, *155*, 195. (c) Moncrieff, D.; Hillier, I. H.; Saunders, V. R.; von Niessen, W. *Inorg. Chem.* **1985**, *24*, 4247.

[32] (a) Cooper, G.; Green, J. C.; Payne, M. P. *Mol. Phys.* **1988**, *63*, 1031. (b) Cooper, G.; Green, J. C.; Payne, M. P.; Dobson, B. R.; Hillier, I. H. *J. Am. Chem. Soc.* **1987**, *109*, 3843.

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[34] Kitagawa, S.; Moroshima, I.; Yoshikawa, K. *Polyhedron* **1983**, *2*, 43.

[35] Fragalà, I.; Condorelli, G.; Tondello, E.; Cassol, A. *Inorg. Chem.* **1978**, *17*, 3175.

[36] The comparison of the present PE data with those of middle and late metal $M(acac)_2$ (M = Mn, Co, Ni, Cu) complexes[34] does not represent a simple task because the spectra of these complexes have been object of only qualitative assignments. In addition, the low PE region (<12 eV) present several features which might be due[12,31b] to the ionizations of filled metal-d orbitals. Further studies combining He I/He II and ab initio calculations are in progress.

Table 3. Comparison of Calculated and Experimental IEs (in eV) for VO(acac)$_2$

		VO(acac′)$_2$				VO(acac)$_2$			
		ΔSCF		CI				relative intensity[c]	
state	dominant character	singlet	triplet	singlet	triplet	estd CI[a]	exptl[b]	He I	He II
A$_1$	$d_{x^2-y^2}$	10.43		10.70 (8.30)[d]		10.19 (7.79)[d]	7.40 (**x**)	0.16	0.34
B$_2$	π_3	9.11	9.10	8.78	8.77 (8.65)[d]	8.25 (8.13)[d]	8.51 (**a**)	1.00	1.00
A$_1$	π_3	9.41	9.39	9.14	9.14	8.58	8.79 (**b**)	0.60	0.65
B$_1$	n_-	11.43	11.22	10.17	10.05	9.43	9.48 (**c**)	1.11	0.98
A$_2$	n_-	12.01	11.82	10.82	10.67	10.07	9.93 (**d**)	1.03	0.79
B$_1$	π(V−O)			11.93	11.81	11.31	10.33 (**e**)	0.95	1.16
B$_2$	π(V−O)			12.00	11.87	11.38	10.88 (**f**)	0.98	1.70
B$_2$	n_+			12.54	12.25	11.63	11.16 (**f′**)	0.88	1.18
A$_1$	σ(V−O)			12.92	12.51	12.00	11.65 (**g**)	0.87	1.11

[a] Estimated CI IEs for VO(acac)$_2$ are obtained from CI IEs for the model VO(acac′)$_2$ reduced by the calculated energy shift due to the methyl groups. [b] Lettering in parentheses refer to the band labels in Figure 4. [c] The intensity of band **a** has been taken as the reference. [d] Calculated CI IE value including 18/10 MOs.

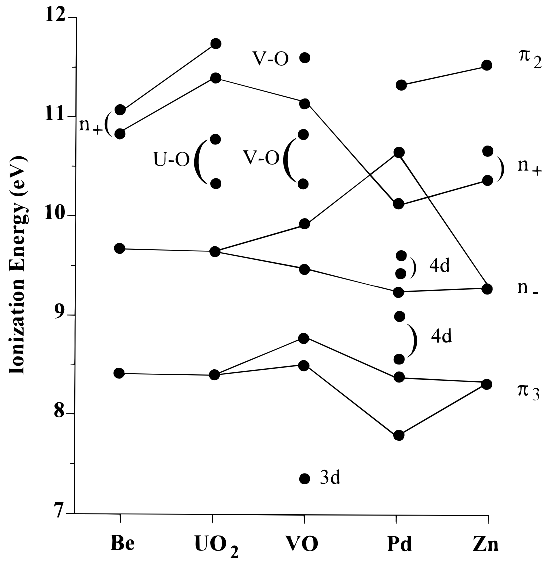

Figure 5. Ionization energies of bis(acetylacetonato)metal complexes.

lower IE, while the more internal component of the n_- orbital set is found considerably higher in IE.[12] The lower IE shift of the π_3 is due to an antibonding four-electron−two-orbital interaction involving the π_3 orbital and the more internal filled d_{xz} orbital,[12,31b] while the higher IE shift of the n_- component is due to the stronger stabilizing interaction with the d_{xy} empty orbital (vide infra). Finally, the π axial V−O ionizations are found close to the IEs of the U-O MO ionizations in the UO$_2$(acac)$_2$.[35,37]

Conclusions

This paper presents a detailed investigation of the electronic structure of the VO(acac)$_2$ molecule. Theoretical ab initio data have provided an accurate description of the metal−ligand bonding and of several physicochemical observables of VO(acac)$_2$. In particular, a CI treatment has allowed a complete assignment of the low IE region of the PE spectrum and has provided a very good fitting of frequencies associated with "d−d" and CT optical transitions.

The V−O bonding is axial in nature. It possesses a partial triple-bond character thus involving the O_{2p} AOs and the d_{z^2} orbital for the σ bond, and the d_{xz} and d_{yz} orbitals for π bonds. The equatorial bonding with the chelating ligands is mostly σ in nature mostly involving the n_- and the V $3d_{xy}$ orbital which by symmetry cannot be involved in the axial bonding. Furthermore, theoretical data evidence additional equatorial bonding effects involving the oxovanadium orbitals. These interactions are better considered in terms of three-orbital−four-electron stabilizing interactions which further reinforce both the axial and the equatorial bonds.

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(37) Note that, additional axial U−O ionizations were assigned together with n_- ionizations.[35]