Theoret. chim. Acta (Berl.) 9, 390—400 (1968)

Semi-Empirical Molecular Orbital Computations

VII. The Electronic Structure of Vanadyl Pentahydrate*

L. G. VANQUICKENBORNE and S. P. McGLYNN

Coates Chemical Laboratories, The Louisiana State University

Received November 6, 1967

A number of Wolfsberg-Helmholz (W–H) type calculations for $VO(H_2O)_5^{++}$ are reported. The aim of the work is twofold: to test the viability of single Slater type mimics of SCF orbitals, and to remove a number of the more drastic assumptions in the original Ballhausen-Gray (B–G) calculations. It is shown that single Slater type orbitals may be obtained in such a way as to more or less reproduce results of W–H calculations using SCF-functions. It is shown that removal of B–G approximations does not change the relative one-electron MO ordering of the B–G scheme; however, the energy gaps between the levels are changed considerably. The effects of displacing the vanadyl group from the equatorial plane are shown to be important.

Eine Anzahl von Wolfsberg-Helmholz (W–H) Rechnungen für $VO(H_2O)_5^{++}$ sind durchgeführt worden, um einerseits SCF-adjustierte einfache Slaterfunktionen zu testen und andererseits eine Anzahl von Vereinfachungen der ursprünglichen Rechnungen von BALLHAUSEN u. GRAY (B–G) zu eliminieren. Es zeigt sich, daß es einfache Slaterfunktionen gibt, die bei Rechnungen nach W–H ähnliche Ergebnisse wie SCF-Funktionen liefern, und daß Rechnungen mit und ohne den Näherungen von B–G die gleiche Reihenfolge der MOs, aber verschiedene Einteilchenenergien liefern. Die Verschiebung der Vanadylgruppe aus der horizontalen Ebene heraus beeinflußt die Elektronenstruktur stark.

Un nombre de calculs d'après Wolfsberg-Helmholz (W–H) est éxecuté sur $VO(H_2O)_5^{++}$ pour tester des fonctions simples de Slater représentantes des orbitales SCF, et pour éliminer un certain nombre d'hypothèses du calcul original de BALLHAUSEN-GRAY (B–G). Il est démontré que des simples STO sont obtenables qui produisent environ les resultats d'un calcul W-H à l'aide des fonctions SCF, et que les calculs soit avec soit sans approximation B-G donnent le même ordre de MO mais une énergie différente. L'effet de délocalisation de la group Vanadyl du plan horizontal est montré d'être très important pour la structure électronique.

Introduction

The molecular orbital treatment of $VO(H_2O)_5^{++}$ by BALLHAUSEN and GRAY [1] has served as model and guide for most discussions of vanadyl-complexes [2, 3], it has been used for the description of vanadium sites in glasses [4], and it has been extended to provide discussion of chromyl- and molybdenyl-complexes [5].

The Ballhausen-Gray calculation, however, involves a rather large number of approximations, and it seems proper to scrutinize these approximations further. In the light of some recent developments in MO-theory on the one hand, and of the increase in experimental knowledge on the other hand, a number of points should be examined critically. First of all, an alternative expression for the resonance

---

* This work was supported by research grants from the United States Atomic Energy Commission — Biology Branch and The National Science Foundation.

integral has been proposed [6]; this expression is probably somewhat better than the usage of the geometric mean between the two relevant Coulomb integrals [7]. Secondly, it is now possible to perform the calculations without the Ballhausen-Gray *a priori* assumptions as to the hybridisation of the atomic orbitals or the pairing of ligand with metal orbitals. Thirdly, it has recently been suggested [8] that the geometry of the vanadyl-water complex is slightly different from that previously assumed. Fourthly, the evaluation of the electron repulsion integrals necessary to proper spectroscopic correlation must be reconsidered or, at least, criticized.

Method

The method used has been described in detail elsewhere [9]: a Wolfsberg-Helmholz type calculation was carried through until self-consistency was reached with respect to charge and configuration. Use was made of the rotationally invariant version [7] of the equation

$$H_{ij} = \tfrac{1}{2} (2 - | S_{ij} |) (H_{ii} + H_{jj}) S_{ij} \tag{1}$$

where H and S are matrix elements of the hamiltonian and overlap operators, respectively [6]. The orbital exponents of the Slater atomic orbitals were constructed to mimic the overlap properties of the SCF functions [10, 11] over a range of representative bond distances. One of the Slater mimics used the proper quantum number, whereas an alternative Slater mimic was engineered to use a quantum number one less than that appropriate to the orbital in question. This latter method has been reported [9, 12] to yield a better match over a larger range of bond lengths than does the former. For the sake of comparison, a calculation was performed using the "correct" SCF-overlaps, thus bypassing the problem of selecting orbital exponents altogether; at the same time, comparison of these various calculations should test the propriety of using Slater mimics at all. Unlike the Ballhausen-Gray calculation, no assumptions were made concerning bonding

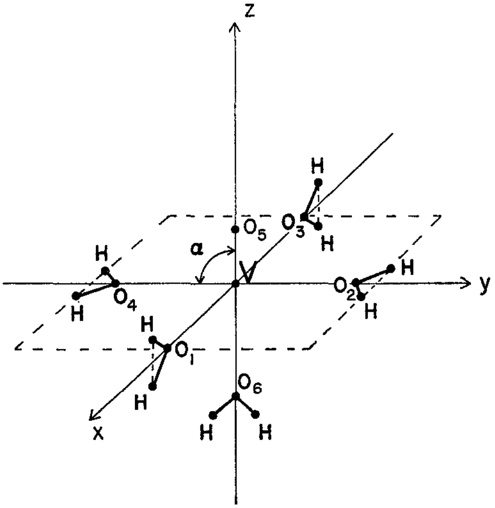

Fig. 1. Assumed C_{2v}-symmetry of the vanadyl-water complex

Table 1. *Charge Distribution at Self-Consistency in the* $VO(H_2O)_5^{++}$ *Complex at* $\alpha = 90°$

A The Ballhausen-Gray scheme (for comparison purposes).

B Overlap matching against SCF-orbitals for neutral atoms, using the correct principal quantum numbers.

C As B, but using (fictitious) smaller quantum numbers (*2d*, *1p*).

D As C, but matching against SCF-orbitals for atoms carrying the charge obtained at self-consistency in the previous case C.

E Using the "correct" (i.e., atomic) SCF-overlaps for neutral atoms[a].

Atom	Method A	B	C	D	E
V	+0.97	+0.86	+0.86	+0.82	+0.83
O	−0.60	−0.15	−0.19	−0.19	−0.21
$5(H_2O)$	+1.63	+1.29	+1.33	+1.37	+1.38

[a] The metal orbitals [11] were "average-of-configuration" wavefunctions; the ligand orbitals [10] could be taken to correspond to any one of the states belonging to a given configuration; however, the resulting uncertainty in the overlap integrals amounted to only a few percent.

possibilities or hybridizations of atomic orbitals. The point group of the complex consequently was C_{2v} (see Fig. 1) as opposed to C_{4v} in an *a priori* hybridized scheme The angle α between the VO-axis and the four equatorial H_2O–V axes was varied between 90° and 105°; Ballhausen and Gray used 90°, while SELBIN et al. [8] recently suggested a value of about 100°. The V–O bond length was 1.67 Å; the V–OH_2 bond length was 2.30 Å for equatorial waters and 2.4 Å in the axial direction. The effects of variation of these bond lengths will be considered briefly.

Results and Discussion

a) Comparison of Different Computations at $\alpha = 90°$

Table 1 contains the self-consistent charge distribution in the complex (at $\alpha = 90°$) resulting from four slighly different calculations. The four different computational approaches, B through E, agree very closely with each other and do not differ too much from case A (BALLHAUSEN and GRAY): the metal has a positive charge of about +1 (as compared to +4 in the crystal field picture), the vanadyl oxygen is negative and the five water molecules slightly positive. The most noticeable difference is the prediction of a considerably smaller negative charge on the vanadyl-oxygen than that found by BALLHAUSEN and GRAY: an experimental determination of the dipole moment is needed to decide which one of the two situations corresponds most closely to reality.

Fig. 2 shows the energy levels of the $VO(H_2O)_5^{++}$ complex at $\alpha = 90°$ for the same four cases; again, the Ballhausen-Gray scheme is given for the sake of comparison. The most striking feature is that the sequence of levels is identical in all cases (the cross-over between B and C is insignificant). The splitting of the *e* MO into $b_1 + b_2$ MO's (reduction of $C_{4v} \rightarrow C_{2v}$) amounts to a few 100 cm^{-1} for e_π^* and to a few 1000 cm^{-1} for e_π. In solution, however, one may expect a free rotation,

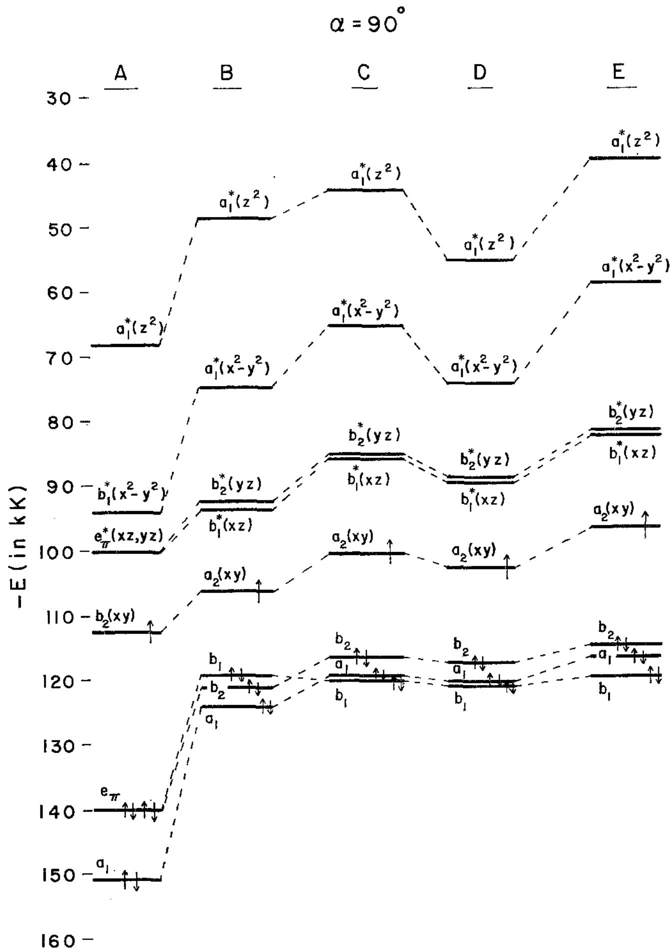

Fig. 2. Energy levels of the $VO(H_2O)_5^{++}$ complex at $\alpha = 90°$. A, B, C, D, and E have the same meaning as they do in Table 1. Note that the BALLHAUSEN-GRAY levels are labelled by C_{4v}-symbols, while all the other levels are labelled by C_{2v}-symbols

resulting in one broadened level (effective C_{4v}-symmetry). In the following, we shall use the C_{4v}-notation consistently.

The MO energy diagram does not differ appreciably for cases A, B, C or D: if there are shifts, all the levels tend to shift in the same direction, so that the same gross features are found in any one of the four schemes. Obviously, the improvements obtained by changing the principal quantum number of the Slater mimic, or by taking the "correct" SCF-overlaps, or by accounting for the effects of charge in the overlap calculations, do not affect the final results to any great extent. To some degree the use of Slater mimics is thereby vindicated.

The most important single point is that the MO energy gaps $e_\pi - b_2$ and $a_1 - b_2$ obtained by us are considerably smaller than those found by BALLHAUSEN and GRAY; on the other hand, we find the gaps $b_2 - b_1^*$ and $b_2 - a_1^*$ to be larger. It is of interest to compare the corresponding wavefunctions; this is done in Table 2.

Table 2. *Energies (in* cm^{-1}*) and Wavefunctions at* $\alpha = 90°$ *for the* $VO(H_2O)_5^{++}$ *Complex*

(All AO's whose coefficients are negligible are omitted. The wavefunctions given here are not exactly the wavefunctions obtained by solving the eigenvalue problem; since the latter possess C_{2v}-symmetry, mean values were taken between those AO-coefficients which are required to be identical in C_{4v}. Consequently, the eigenfunctions which we report here cannot be expected to be part of a perfectly orthonormal set.

	This paper (case B)	E (cm^{-1})	BALLHAUSEN and GRAY [1]	E (cm^{-1})
a_1	$(0.15)\ 3d_{z^2} - (0.06)\ 4p_z$ $-(0.04)\ 2s_5 - (0.57)\ 2p_{z5}$ $-(0.16)\ 2s_6 - (0.29)\ 2p_{z6}$ $-(0.25)\ (2p_{z1} + 2p_{z2} + 2p_{z3} + 2p_{z4})$	−124100	$(0.15)\ 4p_z$ $-(0.47)\ 2s_6 - (0.82)\ 2p_{z6}$	−150750
e_π	$(0.08)\ 3d_{xz} + (0.37)\ (2p_{x5})$ $-(0.30)\ (2p_{z1} - 2p_{z3}) + (0.48)\ (2p_{x6})$	−120540	$(0.45)\ 3d_{xz} + (0.83)\ 2p_{x5}$	−140026
	$(0.08)\ 3d_{yz} + (0.37)\ (2p_{y5})$ $-(0.30)\ (2p_{z2} - 2p_{z4}) + (0.48)\ 2p_{y6}$		$(0.45)\ 3d_{yz} + (0.83)\ 2p_{y5}$	
b_2	$(0.93)\ 3d_{xy}$ $-(0.18)\ (2p_{y1} + 2p_{x2} - 2p_{y3} - 2p_{x4})$	−106060	$(1.00)\ 3d_{xy}$	−112924
e_π^*	$(0.86)\ (3d_{xz}) - (0.67)\ (2p_{x5})$ $-(0.09)\ (2p_{z1} - 2p_{z3}) + (0.11)\ (2p_{x6})$	− 91010	$(0.91)\ 3d_{xz} - (0.57)\ 2p_{x5}$	−100422
	$(0.86)\ (3d_{yz}) - (0.67)\ (2p_{y5})$ $-(0.09)\ (2p_{z2} - 2p_{z4}) + (0.11)\ (2p_{y6})$		$(0.91)\ 3d_{yz} - (0.57)\ 2p_{y5}$	
b_1^*	$(0.96)\ 3d_{x^2-y^2}$ $-(0.18)\ (2s_1 - 2s_2 + 2s_3 - 2s_4)$ $+(0.28)\ (2p_{x1} - 2p_{y2} - 2p_{x3} + 2p_{y4})$	− 75020	$(0.95)\ 3d_{x^2-y^2}$ $-(0.28)\ (2s_1 - 2s_2 + 2s_3 - 2s_4)$ $+(0.48)\ (2p_{x1} - 2p_{y2} - 2p_{x3} + 2p_{y4})$	− 94130
a_1^*	$(0.94)\ 3d_{z^2}$ $-(0.20)\ (4s) - (0.25)\ 2p_z$ $+(0.18)\ (2s_1 + 2s_2 + 2s_3 + 2s_4)$ $-(0.17)\ (2p_{x1} + 2p_{y2} - 2p_{x3} - 2p_{y4})$ $-(0.22)\ (2s_5) + (0.49)\ 2p_{z5}$ $-(0.21)\ (2s_6) - (0.17)\ 2p_{z6}$	− 48540	$(0.70)\ 3d_{z^2}$ $+(0.70)\ 4s$ $-(0.27)\ 2s_5 + (0.56)\ 2p_{z5}$	− 68160

The MO's obtained by us are considerably more complex than those postulated by BALLHAUSEN and GRAY. Thus, while a_1 and e_π are essentially bonding, they do contain a number of atomic orbitals in *anti*-bonding conditions. For example, the overlaps between $3d_{z^2}$ and $(-2p_{z6})$, or between $3d_{xz}$ and $(2p_{z3}-2p_{z1})$, are negative; thus, strong destabilization of the a_1 and e_π energy levels occurs relative to their energies in the simplified *a priori* bonding scheme of BALLHAUSEN and GRAY — hence the smaller gaps in our MO energy scheme.

The effect of the π-interactions between metal and ligand is seen to be less important in e_π^* than in e_π; in the a_1^*-orbital, on the other hand, inclusion of the σ-interaction between the equatorial ligands and the metal results in a very strongly antibonding contribution to the energy.

An interesting consequence implicit in the expression of Table 2 concerns the transition $e_\pi \rightarrow e_\pi^*$, which is usually interpreted as a simple charge transfer transition from the vanadyl oxygen towards the metal. According to the wavefunctions obtained by us, this transition should be considered as a charge transfer from the water ligands towards the vanadyl group, with the transfer to the vanadium much larger than that to the vanadyl oxygen.

It may be verified from Table 2 that the hybridization resulting from the solution of the eigenvector problem is markedly different from the hybridization obtained by minimizing the ratio VSIE/S (per BALLHAUSEN and GRAY). The σ_5-hybrid on the vanadyl oxygen, for instance, is found to have a good deal more p-character, while the sd_{z^2}-hybrid on vanadium has far more d-character than is given by the VSIE/S minimization procedure. Usage of the Ballhausen-Gray hybrids as a basis for further calculation must be considered a somewhat uncertain procedure, unless these calculations happen to be rather insensitive to the actual values of the coefficients (see e.g. the determination of ESR-parameters by HECHT and JOHNSTON [4]).

In summary, the differences between the present energy level scheme and the Ballhausen-Gray scheme can be traced back to the *a priori* assumptions concerning bonding patterns and hybridizations made by these authors. The different H_{ij}-expression, or the procedure for calculating overlaps (provided they approximate SCF-overlaps fairly well), seem to be less important. Whatever method one uses, as long as one includes all the orbitals, and one lets an interaction occur whenever the overlap is significant, one obviously finds an energy level scheme as shown in Fig. 2, B through E*.

b) *Influence of the Geometry*

The angle α (where α is defined as $\mathrm{O{-}V{-}(OH_2)_{eq}}$ and where the subscript "eq" means any of the four equatorial water molecules) was varied between 90° and 105°. The energy level diagrams are shown in Fig. 3. The effect of angle variation is significant only in the non-occupied MO levels: relative to the b_2-orbital, e_π^* increases, while b_1^* and a_1^* decrease in energy.

When α increases, it becomes possible for the $3d_{xz}$, $3d_{yz}$ orbitals to overlap effectively with the group orbitals $(2p_{x1}+2p_{x3})$, $(2p_{y2}+2p_{y4})$. The total overlap, say, of $3d_{yz}$ with $2p_{y2}$ as a function of α is:

$$S = \cos\alpha \cos 2\alpha\, S(2p\pi, 3d\pi) - \frac{\sqrt{3}}{2} \sin\alpha \sin 2\alpha\, S(2p\sigma, 3d\sigma)$$

showing that both σ and π-interactions are involved; the coefficient for σ-overlap is about twice as large as the coefficient for π-overlap. In this manner, most of the variations exhibited in Fig. 3 may be rationalized.

---

* However, this assertion is not generally correct; for a number of small molecules (e.g., ethylene), the results are known to be quite sensitive to the precise value of the individual overlap integrals.

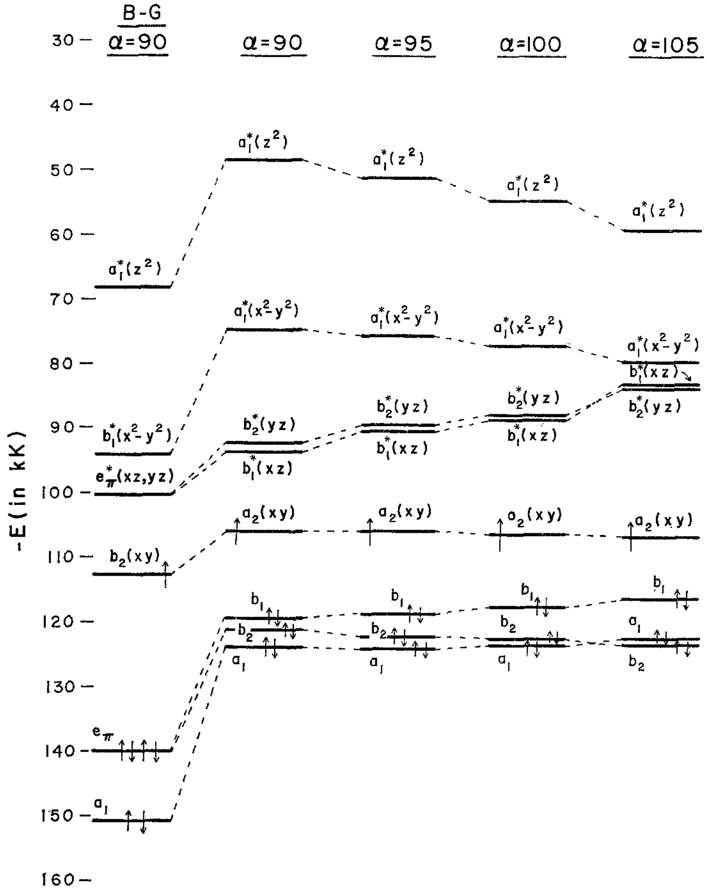

Fig. 3. Effect of α-variation on the energy levels. All calculations correspond to case B. The Ballhausen-Gray scheme is given for comparison and is shown in the leftmost location

The a_1^*- and b_1^*-levels are stabilized with increased α because the involvement of the equatorial ligands (*via* σ-overlaps) obviously decreases considerably. Contrary to the suggestion by Selbin et al. [8], however, it seems that at α ~100°, the e_π^*-level is still well below b_1^*; the total angle variation of 15 degrees results in energy level shifts of 5000 to 10000 cm^{-1}.

Accordingly, it becomes somewhat objectionable to compare, as such, the spectra of different vanadyl-complexes, or even of a given complex in different solvents; indeed, quite small changes in the angle α can result in spectroscopic band shifts of a few kilokayser.

Variation of bond lengths within the limits of precision of the X-ray data (and even outside of these limits) does not produce, in most cases, changes in the overlap integrals of the same magnitude as the change caused by angle variation. A decrease of the distance $V-(H_2O)_{eq}$ from 2.30 Å to a lower value of 2.1 or 2.0 Å does result in a considerable destabilization of the $b_1^*(x^2-y^2)$ level; however, such a larger bond length change would appear to be ruled out by EPR-data.

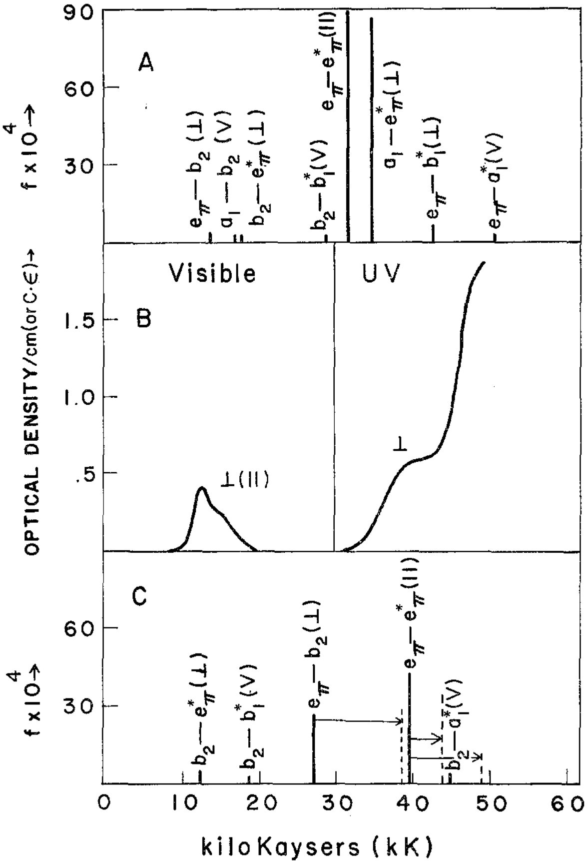

Fig. 4A. One electron transition energies, oscillator strengths and polarizations predicted by the present calculations ($\alpha = 100°$). The symbol V means vibronic. B The electronic spectrum of $VOSO_4 \cdot 5H_2O$ in aqueous solution according to BALLHAUSEN and GRAY [1]. Left (IR and visible spectrum): concentration C of complex is 0.0237 M, H_2SO_4 concentration is 0.1 M; right (ultraviolet spectrum): $C = 0.00237$ M, H_2SO_4 concentration is 0.01 M. C One electron transition energies (solid lines) and state transition energies (dashed lines), oscillator strengths and polarizations obtained by BALLHAUSEN and GRAY. The symbol V means vibronic

c) Spectroscopic Assignments

Fig. 4B shows the electronic absorption spectrum of $VOSO_4 \cdot 5H_2O$ in aqueous solution, according to BALLHAUSEN and GRAY; their calculated oscillator strengths and their experimental and theoretical polarization results are shown in Fig. 4C.

Among the different energy level schemes of Fig. 3, the one at $\alpha = 100°$ seems to provide the best overall agreement with experiment, as has been previously suggested [8]. Fig. 4A shows the one-electron MO-transitions corresponding to the situation at $\alpha = 100°$, together with the predicted polarization and oscillator strengths; the latter are also given in Table 3.

Comparison of Figs. 4A and C reveals that the difference between the Ballhausen-Gray calculation and the present treatment is more pronounced than

Table 3. *Oscillator Strengths and Polarizations (C_{4v}-Notation)*

Transition	Oscillator Strengths		Predicted Polarization
	This Paper ($\alpha = 100°$)	BALLHAUSEN-GRAY	
"d–d" transitions			
$^2B_2 \to {}^2E(xy \to xz, yz)$	$(1.04)\,10^{-4}$	$(3.9)\,10^{-4}$	$\perp (x, y)$
$^2B_2 \to {}^2B_1(xy \to x^2 - y^2)$	f	f	—
$^2B_2 \to {}^2A_1(xy \to z^2)$	f	f	—
"charge transfer"			
$^2B_2 \to {}^2E$ (I) $(e_\pi \to xy)$	$(3.56)\,10^{-4}$	$(26.4)\,10^{-4}$	$\perp (x, y)$
$^2B_2 \to {}^2A_1(a_1 \to xy)$	f	f	—
$^2B_2 \to {}^2B_2$ (I) $(e_\pi \to xz, yz)$	0.45	$(44.7)\,10^{-4}$	$\parallel (z)$
$^2B_2 \to {}^2B_2$ (II)	0.15	—	$\parallel (z)$
$^2B_2 \to {}^2E$ (II) $(a_1 \to xz, yz)$	$(66)\,10^{-4}$	—	$\perp (x, y)$
$^2B_2 \to {}^2E$ (III)	$(22)\,10^{-4}$	—	$\perp (x, y)$
$^2B_2 \to {}^2E$ (IV) $(e_\pi \to x^2 - y^2)$	$(6)\,10^{-4}$	—	$\perp (x, y)$
$^2B_2 \to {}^2E$ (V)	$(2)\,10^{-4}$	—	$\perp (x, y)$

would appear at first sight from Figs. 2 and 3. Indeed, certain one-electron transitions are positioned in altogether different regions of the spectrum by the two schemes, and some intensities (as, for instance, that of $e_\pi \to b_2$) are very different.

As can be seen from Fig. 4A, the $d - d$ splits are found to be very large. They would become even larger if instead of Eq. 1 a geometric mean expression were used for H_{ij} [13]. This result would seem to refute the assignment of ORTOLANO et al. [14] who placed all $d - d$ transitions below 20000 cm^{-1} for VO(acac)$_2$. The $b_2 \to e_\pi^*$ transition is predicted to lie in the low energy region and $b_2 \to a_1^*$ transition to be buried under the high energy bands. The forbidden transition $b_2 \to b_1^*$ $(xy \to x^2 - y^2)$, which should be quite sensitive both to bond length and angle α, falls between these two absorption regions; EPR measurements (*vide infra*) suggest that this transition probably lies in the low energy region, but this assignment is not as strongly supported by MO-calculation as was originally claimed.

Assignment of the charge transfer transitions requires inclusion of electron repulsion corrections. In a charge self-consistent calculation, one might expect these corrections to be less important than in the simpler extended Hückel calculations. At any rate, the most obvious suggestion would seem to assign both $^2B_2 \to {}^2E$(I) $(e_\pi \to b_2)$ and $^2B_2 \to {}^2A_1(a_1 \to b_2)$ to the low energy region, since they have the correct position (if the electron repulsion correction is small), as well as the correct intensity and polarization*. The high energy region would then consist essentially of the $^2B_2 \to {}^2B_2(e_\pi \to e_\pi^*)$, $^2B_2 \to {}^2E(a_1 \to e_\pi^*)$ and $^2B_2 \to {}^2E(e_\pi \to b_1^*)$ transitions. These assignments would, indeed, explain the observation, at low temperature, of more than two bands in the low energy region [14].

---

* Indeed, the additional 11700 cm^{-1} which BALLHAUSEN and GRAY add to the one-electron transition energy of $e_\pi \to b_2$ seems exceedingly high. It is true that the b_2-orbital is more localized than the e_π-orbital, but the latter contains $2p$-orbitals, for which the F-integrals are much larger than for d-orbitals.

There are, however, some very serious objections against these assignments. First, it has been reported [14] that the whole low energy band system in $VO(acac)_2$ disappears, presumably because of oxidation, when a solution is allowed to stand for a number of hours. If this process is properly described as a simple removal of an electron from the b_2 orbital (without concomitant changes in geometry or electronic structure), this observation supports the conclusion that the low energy absorption region is entirely made up of $d - d$ transitions. However, a much more serious objection is that in all known vanadyl complexes, the absorption spectrum seems always to possess a few low intensity bands in almost precisely the same region (10 to 18 kK). Charge transfer bands, on the other hand, are expected to shift over a much larger energy range; and, indeed, the bands in the high energy region do shift ~10 to 15 kK from one complex to another. Thus, it seems doubtful to suppose that the low energy bands are of a significant charge transfer nature.

Therefore, we now differentiate between two aspects of the Ballhausen-Gray interpretation of the vanadyl pentahydrate spectrum. Firstly, their assignment of the observed spectrum to various transition types seems reasonable (but not necessarily correct) in view of the available data. It is our contention that the second aspect of their work, namely the extent to which computation substantiates these assignments, is not as definitive as is usually supposed. Relative to the B–G assignments, the present computations position all charge transfer bands at too low an energy. However, relative to the B–G calculations, we predict less pronounced charge transfer character for all these transitions: in the present work *all* MO's possess non-negligible amplitudes on both metal and water ligands, which immediately reduces the charge transfer character considerably. We can restore agreement with the B–G assignments only if we exclude enough pairing possibilities so as to generate more localized MO's. It is in this way, in fact, that BALLHAUSEN and GRAY substantiate their assignments. However, in doing so, the e_π, b_2 and e_π^* MO's become devoid of amplitudes on the water ligands. Thus, while accounting for band positions (after the further introduction of some debatable electron repulsion corrections), they predict these band positions to be almost insensitive to the ligands, — the opposite, of course, is known to be the case.

It seems to us that the present calculations predict the proper form of the wavefunctions and lead to correct predictions as to the ligand dependence of the spectrum. On the other hand, the positions of the energy levels is not predictable with any great accuracy; indeed, only the relative order appears to be meaningful.

d) Magnetic Properties

The magnetic properties of the complex can be explained reasonably satisfactorily using either set of calculations. In the expression

$$g_{ij} = 2\,(\delta_{ij} - \lambda \Lambda_{ij})$$

we find the tensor components Λ_{ij} to be somewhat smaller than BALLHAUSEN and GRAY, because the perturbation gaps in our case are larger (especially for b_1^*). On the other hand, as was pointed out by KIVELSON and LEE [15], the value of the appropriate spin-orbit coupling constant λ should be somewhat larger than the value of 135 cm^{-1} used previously [1]; indeed, the 4*s*-orbital has a non-zero population even in the ground state, and the experimental value of λ_{3d} for a $3d^{n-1}\,4s$ configuration is larger than that for the corresponding $3d^n$-configuration [16].

Conclusions

The Ballhausen-Gray interpretation of the vanadyl spectra, though seemingly in good agreement with experiment, is less substantiated by molecular orbital theory than is usually supposed. If one assumes bonding simply and only to the extent that the orbitals overlap, the $d - d$ transitions resulting from our calculations tend to be too high in energy, while the charge-transfer transitions tend to be too low in energy if one accepts the B–G assignment. The orbital pairing restrictions, which are apparently useful to obtain better agreement with experiment, do not derive from chemical intuition and only in part from analogies with crystal field theory.

As to the extension of any presently available MO scheme to other complexes, or even to the same complex in different solvents, a careful consideration of the observed shifts is necessary in the light of possible variations of the angle α.

Acknowledgements. The authors would like to acknowledge some very helpful suggestions from Dr's. MINORU KINOSHITA and DANIEL CARROLL. We also thank Dr. JOEL SELBIN for making available to us his paper [8] prior to publication.

References

1. BALLHAUSEN, C. J., and H. B. GRAY: Inorg. Chem. **1**, 111 (1962).
2. SELBIN, J.: Coord. Chem. Rev. **1**, 293 (1966).
3. ZERNER, M., and M. GOUTERMAN: Inorg. Chem. **5**, 1699 (1966).
4. HECHT, H. G., and S. T. JOHNSTON: J. chem. Physics **46**, 23 (1967).
5. GRAY, H. B., and C. R. HARE: Inorg. Chem. **1**, 363 (1962).
6. CUSACHS, L. C.: J. chem. Physics **43**, 5157 (1965).
7. CARROLL, D. G., and S. P. McGLYNN: J. chem. Physics **45**, 3827 (1966).
8. SELBIN, J., G. MAUS, and D. L. JOHNSON: J. Inorg. Nucl. Chem. In press.
9. CARROLL, D. G., and S. P. McGLYNN: Inorg. Chem. In press.
10. CLEMENTI, E.: Tables of atomic functions. Supplement to paper in IBM J. Res. Develop. **9**, 2(1965).
11. RICHARDSON, J. W., W. C. NIEUWPOORT, R. R. POWELL, and W. F. EDGELL: J. chem. Physics **36**, 1057 (1962); **38**, 796 (1963).
12. CUSACHS, L. C., D. G. CARROLL, B. L. TRUS, and S. P. McGLYNN: Int. J. Quant. Chem. (Slater Issue). In press.
13. FENSKE, R. F.: Inorg. Chem. **4**, 33 (1965).
14. ORTOLANO, T. R., J. SELBIN, and S. P. McGLYNN: J. chem. Physics **41**, 262 (1964).
15. KIVELSON, D., and S. LEE: J. chem. Physics **41**, 1896 (1964).
16. DUNN, T. M.: Trans. Faraday Soc. **57**, 1441 (1961).

Professor S. P. McGLYNN
Coates Chemical Laboratories
The Louisiana State University
Baton Rouge, Louisiana 70803, USA