The Electronic Structure of Organometallic Complexes Involving f-Electrons, II¹ Magnetic Susceptibility and Crystal Field Splitting of Uranium(IV)-tetracyclopentadienide

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Some significant features of the low-energy part of the crystal field (= CF) splitting pattern of the organometallic $5f^2$ -system $(\eta^5\text{-C}_5\text{H}_5)_4\text{U(IV)}$ can be deduced from the temperature dependence of the magnetic susceptibility which has been measured on polycrystalline samples between 1.1 and 298 K. The results of model calculations performed independently on the basis of three different semi-empirical approaches are compatible with the deductions from the experiments and allow estimates of the sign and order of magnitude of quantities like the CF-splitting parameters B_4^0 and B_6^0 viz. the (averaged) angular overlap parameters e_σ and e_π and of the valence state ionisation potential of the $5f$ -electrons. Anticipating a rather weakly perturbed tetrahedral CF, the observed magnetic properties may be satisfactorily simulated if the six lowest-lying first-order CF-states and one common scaling factor are accounted for.

1. Introduction

The quasi-tetrahedral molecular structure of the organometallic actinide complex uranium-tetracyclopentadienide, $(\eta^5\text{-C}_5\text{H}_5)_4\text{U(IV)} = \text{UCp}_4$, which was proposed by FISCHER and HRISTIDU as early as 1962^{2,3} has been recently confirmed by BURNS⁴⁻⁶ by a detailed single crystal X-ray study. Thus, each of the two discrete UCp_4 -molecules composing the tetragonal unit cell (space group $I4_2m$) contains four equivalent, penta-hapto coordinated Cp-ligands, the appropriate rotational arrangements of which give rise to the molecular point symmetry S_4 . In view of these results, the first attempt to

interpret the observed temperature dependence of the magnetic susceptibility (=Sc) of the polycrystalline $[\text{Rn}]5f^2$ -system** in terms of pure T_d -symmetry⁷ is now subject to improvement, although the basic conclusions concerning the origin of the isotropic $^1\text{H-NMR}$ shifts of UCp_4 in solution remain essentially unchanged^{7,8}.

The situation has been somewhat confused by a subsequent Sc-study between $T = 2.6$ and 100 K by KARBAKER *et al.*⁹ who found Curie-Weiss-behaviour up to 25 K, but a practically temperature independent Sc (=TIP) between 60 and 100 K. While these authors have attempted to explain this unusual feature in terms of T_d -symmetry, arguing that a magnetically active electronic ground state be closely followed by a first excited, non-magnetic crystal field (=CF)-state ($\Delta E = 30 \text{ cm}^{-1}$), we have been unable to construct any kind of CF-splitting

* As BURNS has pointed out, the occurrence of equal quantities of the two S_4 -enantiomers would crystallographically correspond to one singular species with the molecular symmetry D_{2d} ⁵.

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** The observation of Curie-Weiss-behaviour between $T = 90$ and 296 K, corresponding formally to 2.78 B.M. was originally associated with a simple two-electron spin-only system^{2,3}.

pattern which would account for the experimental findings.

In view of these apparent inconsistencies we have undertaken a complete re-examination of the temperature dependence of the Sc of UCp_4 , which now covers the entire range from 1.1 up to 298 K, and involves a particularly careful analysis of the low-temperature range between 1.1 and 10 K.

2. Temperature Dependence of the Magnetic Susceptibility

Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility χ^{-1} (a) *viz.* of the squared effective magnetic moment, $\mu_{\text{eff}}^2 = 8\chi T$ (b). The circles correspond to the observed data, the two full-line curves to the best fit of the experimental findings calculated on the basis of Eq. (15).

The curves (a) and (b) of Fig. 1 embody the results of a total of 105 measurements at 35 different temperatures of samples obtained from large, finely ground octahedral crystals of high-purity UCp_4 , a sample of which had also been subjected to the X-ray study⁵. At each temperature, the magnetic field strength was varied between 2388 and 7959 A/cm*, but throughout the entire temperature range there was no evidence for a field dependence of the Sc. All the results have been corrected for the incremental diamagnetism of the U^{4+} -cation and the four C_5H_5^- -anions.

* According to 3 *viz.* 10 kOe.

As shown by curve (a), substantial TIP with $\chi = 0.018 \text{ cm}^3/\text{mole}$ results at very low temperatures up to 11.5 K, thus immediately revealing the existence of a Zeeman-inactive CF-ground state, which can only contribute to the observed Sc via non-diagonal elements (=NDE) with respect to the magnetic field operator $\beta H(\hat{L} + 2\hat{S})$ between its eigenfunction and those of low-lying excited states. The corresponding μ_{eff}^2/T -diagram (b) confirms this since a relatively steep and strictly linear section of the curve extending up to 17 K is observed, which by extrapolation towards $T=0$ precisely intersects the coordinate origin**. The absence of any field dependence of the Sc, even at the lowest temperatures studied, is in full accordance with the assumption of a non-magnetic ground state and a TIP exclusively due to NDE's¹⁰.

Above 30 K, at least two and at most three different quasi-linear Curie-Weiss-sections*** are found as the temperature is increased in curve (a)****. This suggests that up to room temperature at least two excited CF-states become thermally populated¹⁰. The alternative graphic representation (b) is consistent with this view in that here, within the temperature ranges of the Curie-Weiss-sections no full linearity is apparent. A quasi-linear curve section above 210 K suggests that even up to room temperature second-order Zeeman-interactions between all of the thermally populated CF-states and at least one further, relatively low-lying but still practically unpopulated CF-state play a non-negligible role.

3. General Crystal Field Considerations

The optical absorption spectra of UCp_4 are known to be noticeable simpler than the corresponding spectra of all complexes of the type $(\eta^5\text{-C}_5\text{H}_5)_3\text{UX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{BH}_4$)¹¹, where the CF-symmetry cannot be higher than C_{3v} , so that it may be deduced that the actual symmetry of the CF of UCp_4 should not deviate drastically from T_d . (Considering only the central ion and the ring normals, UCp_4 belongs to the molecular point group T_d ⁴). Therefore it seems tempting for a CF-

** $\mu_{\text{eff}}^2 = (3 \cdot k/N\beta^2) \chi \cdot T = 8.0 \cdot \chi \cdot T$.

*** According to $\chi = C/(T-\theta)$.

**** Linear curve sections are primarily found between $T = 27$ and 83 K [$C = 0.565 \text{ (cm}^3 \cdot \text{grd)}/(\text{mole})$, $\theta = -18^\circ$], between 195 and 298 K ($C = 0.90$, $\theta = -100^\circ$) and possibly also between 100 and 177 K ($C = 0.758$, $\theta = -53^\circ$).

treatment of UCp₄ to adopt a CF-Hamiltonian of the form:

$$H_{CF} = H_{CF}(T_d) + H_{CF}(S_4) \quad (1)$$

assuming a much stronger contribution from the strictly tetrahedral component $H_{CF}(T_d)$ than from the S_4 -component $H_{CF}(S_4)$.

Table I. Correlation of some irreducible representations for the descent of symmetry: $T_d \rightarrow D_{2d} \rightarrow S_4$.

T_d	D_{2d}	S_4
A_1	A_1^{II}	A^{III}
E	A_1^I B_1	A^I B^I
T_1	A_2 E^{II}	A^{II} E^{II}
T_2	B_2 E^I	B^{II} E^I

A strictly tetrahedral CF would split the ionic ground state $^3H_4'$ of the [Rn]5f²-system U⁴⁺ into four CF-states. Considering the correlation table (Table I) for the descent from T_d - to S_4 -(via D_{2d} -) symmetry¹², it appears reasonable to associate the three *viz.* four closely following CF-states already populated at room temperature with some tetrahedral parent states which are, moreover, almost accidentally degenerate. In Table II, the three particular situations are specified in which, according to the familiar Lea-Leask-Wolf (=LLW)-diagram for the pure Russell-Saunders-state 3H_4 (see Fig. 2)¹³ a crossover of the two (or three) lowest CF-states can take place. However, the experimental μ_{eff}^2 -value for room temperature does not match any of the three theoretical μ_{eff}^2 -values which would correspond to the three particular values of the ratio B_4^0/B_6^0 of the two CF-splitting parameters** if accidental degeneracy is required for the CF-states originating from the ideal Russell-Saunders-term 3H_4 only. It is therefore reasonable to assume that substantial "higher-order effects" such as J-mixing *via* the (necessarily strong) CF,

orbital reduction effects etc. might be too important to still maintain the LLW-formalism as a useful approximation¹.

Fig. 2. Lea-Leask-Wolf-diagram of the free ion state 3H_4 .

Table II. Specification of zero-energy crossover points in the Lea-Leask-Wolf-diagram of the 3H_4 -manifold (from first-order CF-calculations).

Accidental degeneracy of states	B_4^0/B_6^0	μ_{eff}^2 (B.M.) ²
$E:T_2$	4.88	7.872
$A_1:T_2$	— 1.94	6.000
$A_1:E:T_1$	— 10.46	8.972

4. Model Calculations for Fictive T_d -Systems

For a further examination whether the above assumption of some rather weakly perturbed and almost (accidentally) degenerate tetrahedral CF-states is compatible with the particular molecular geometry of UCp₄, the ratio B_4^0/B_6^0 was determined on the basis of various semi-empirical model concepts. To begin with, the fictitious, strictly tetrahedral f¹-system (η^6 -C₆H₆)₄M was subjected to model calculations in terms of pure T_d -symmetry which involved essentially the same procedures as outlined in full detail in a recent treatment of the sandwich complex uranocene¹. The radius of the circles circumscribing the C₆-rings was taken equal to that of the C₅-ring within a real Cp-ligand, and the distance $\overline{MC}$ was set equal to the known $\overline{UC}$ -value in UCp₄⁴. The possibility of constructing two strictly tetrahedral but stereochemically non-equivalent conformers***, ****

* The prime signifies the somewhat idealized view adopted by using the Russell-Saunders-symbol 3H_4 .

** The parameters B_n^0 are defined by the following cubic Hamiltonian:
 $H_{CF}(T_d) = B_4^0\beta(O_4^0 + 5 O_4^4) + B_6^0\gamma(O_6^0 - 21 O_6^4)$,
 where the O_n^m -terms are angular momentum operators transforming like the corresponding spherical harmonics and β , γ are operator equivalent factors introduced by STEVENS¹⁴.

*** Conformation A with C₆H₆-rings pairwise converging with corners.

**** Conformation B with C₆H₆-rings pairwise converging with edges.

(which may be transformed into each other by appropriate rotations about the six-fold axes of the cyclic ligands) has required a separate consideration of each conformer.

In view of the current interest in the physical origin and significance of CF-parameter sets playing a dominant role in all parametrized models¹⁵ we have chosen to adopt three different model conceptions for the evaluation of the ratio B_4^0/B_6^0 :

- the electrostatic "point charge model" (=EPC)¹⁶,
- the "angular overlap model" (=AOM)^{17,18} and,
- a simple molecular orbital approach in terms of the Mulliken-Helmholz-Wolfsberg (=MHW-MO)-method.

Whilst the EPC represents the extreme view of purely electrostatic interactions, the AOM and the MHW-MO are modified versions of an alternative view involving essentially covalent interactions (based on the consideration of overlapping orbitals).

- According to the EPC the CF-parameters B_n^0 are given by¹⁶:

$$B_n^0 = A_n^0 \langle r^n \rangle = \frac{4\pi}{2n+1} \sum_j q_j \cdot q \cdot r^{n-1} Y_n^0(\Theta_j; \Phi_j) \cdot \langle r^n \rangle \quad (2)$$

where the $\langle r^n \rangle$'s represent the quantum mechanical expectation values of r^n and $Y_n^0(\Theta_j; \Phi_j)$ results from the insertion of the coordinates Θ_j and Φ_j of the j -th ligand atom into the spherical harmonic $Y_n^0(\Theta_j; \Phi_j)$. The summation j extends over all $j=1$ to 24 ligator (*i.e.* ring carbon) atoms which are assumed to have the effective charge $q_j = 4e/24$ (e = electronic charge). Employing Lenander's numerical values for the $\langle r^n \rangle$ 's²⁰ and the $\overline{UC}$ -distance given by BURNS⁴, the ratio B_4^0/B_6^0 for both conformations turns out to be *ca.* 16 (with B_4^0 and $B_6^0 < 0$). This ratio corresponds to an x -value of -0.90 in the LLW-diagram for the ionic state 3H_4 , thus suggesting the sequence $T_2:E:T_1:A_1$ for the model system $(\eta^6-C_6H_6)_4U(IV)^{4+}$.

- Within the framework of the AOM, all parameters B_n^m can ultimately be formulated as linear combinations of the type¹⁸:

$$B_n^m = \sum_{\lambda} K_{\lambda} \cdot e_{\lambda} \quad (3)$$

where the coefficients K_{λ} depend essentially on the specific geometry of the complex under consideration. The AO-parameters e_{λ} refer to the two-centre-interaction between each of the 24 equivalent ring

carbon atoms and the central metal ion ignoring, for the sake of simplicity, any π -interaction within, and between, the cyclic ligands (*vide infra*). In the present case, where the ring-C-atoms will essentially employ their $2p_z$ -orbitals for covalent bonding we are restricted to $\lambda = \sigma$ and π . By appropriately accounting for the discrete geometries of the two possible T_d -conformations, the two sets of equations which give the energies of the seven f-orbitals in terms of the B_n^m and of the e_{λ} -values, respectively*, have been evaluated by familiar methods^{17,18,20}. The CF-parameters of the two fictive model systems result as follows:

$$\begin{aligned} \text{conformation A: } B_4^0 &= -0.278 e_{\sigma} - 0.138 e_{\pi} \\ B_6^0 &= -0.075 e_{\sigma} + 0.053 e_{\pi} \end{aligned} \quad (4a)$$

$$\begin{aligned} \text{conformation B: } B_4^0 &= -0.293 e_{\sigma} - 0.105 e_{\pi} \\ B_6^0 &= -0.088 e_{\sigma} + 0.024 e_{\pi} \end{aligned} \quad (4b)$$

Since the pairs of linear combinations in (4a) and (4b) are so similar, the transition from the fictive f^1 -system to the two-electron system in question has been carried out with Eq. (4a) only.

A tetrahedral CF splits the ionic Russell-Saunders-ground state 3H_4 into four symmetry determined CF-states, the energies of which are specified in (5).

$$\begin{aligned} E(A_1) &= -1.234 B_4^0 - 6.148 B_6^0 \\ E(E) &= -0.176 B_4^0 + 4.919 B_6^0 \\ E(T_1) &= -0.617 B_4^0 + 0.307 B_6^0 \\ E(T_2) &= +1.146 B_4^0 - 1.537 B_6^0 \end{aligned} \quad (5)$$

Substituting (4a) into (5) yields the corresponding energies in terms of the AO-parameters e_{σ} and e_{π} :

$$\begin{aligned} E(A_1) &= +0.804 e_{\sigma} - 0.155 e_{\pi} \\ E(E) &= -0.320 e_{\sigma} + 0.285 e_{\pi} \\ E(T_1) &= +0.149 e_{\sigma} + 0.101 e_{\pi} \\ E(T_2) &= -0.203 e_{\sigma} - 0.239 e_{\pi} \end{aligned} \quad (6)$$

It is convenient to present the information involved in (6) by an AO-diagram in which the specific CF-energies $E(I_i)$ are plotted (in units of e_{σ}) against the ratio e_{π}/e_{σ} ²¹⁻²³. It is seen that within the range $-1 < e_{\pi}/e_{\sigma} < +1$, which seems particularly relevant for chemical arguments²⁴, only the potential tetrahedral ground states E and T_2 have a chance of approaching each other in the sense of becoming accidentally degenerate (see Fig. 3).

* In some instances the relevant relations found in the literature for π -interactions had to be extended with respect to the axial and cubic set of the f-orbitals²¹.

Fig. 3. Angular overlap diagram of the fictive tetrahedral complex $(\eta^6\text{-C}_6\text{H}_6)_4\text{U}^{4+}$ (conformation A).

c) Within the framework of the MHW-MO approach¹⁹ the orbital energies $E(\gamma_r)$ of the fictive tetrahedral model complex (f^1 -system) result from the diagonalisation of three secular determinants of the type:

$$|H_{ij}(\gamma_r) - G_{ij}(\gamma_r) \cdot E(\gamma_r)| = 0 \quad (7)$$

of the orders 2, 3 and 4, respectively. Table III indicates the number and origins of the various linear combinations of the four C₆H₆-ligands which have been explicitly considered (only the b_2 -combination of the C₆H₆-ring was ignored). The geometric factors involved in the six different group overlap integrals $G_{ij}(\gamma_r)$ were determined by standard procedures²⁵ and appropriately combined with the two-centre overlap integrals S_λ which were also used in two MO-treatments of uranocene^{26,1}. The resonance integrals $H_{ij}(\gamma_r)$ were approximated by the expression:

$$H_{ij}(\gamma_r) = G_{ij}(\gamma_r) \cdot [H_{ii}(5f) + H_{jj}(\gamma_r)] \quad (8)$$

where the Coulomb integrals $H_{jj}(\gamma_r)$ of the π -orbitals of the ligands C₆H₆ were assumed to be equal to those used in an earlier treatment of the dibenzene chromium system²⁷.

The value of the Coulomb integral $H_{ii}(5f)$ of the 5f-orbitals is expected to lie between those of the d-transition elements [$H_{ii}(3d) = -6$ to -9 eV]²⁵ and those of the lanthanides [$H_{ii}(4f) = -11$ to -24 eV]²⁸. Owing to the lack of reliable data for U(IV) we have carried out a series of model calculations by varying the value of $H_{ii}(5f)$ systematically from -8 to -12 eV. In all instances B_4^0

Table III. Correspondence of ligand linear combinations and metal f-orbitals in $(\eta^6\text{-C}_6\text{H}_6)_4\text{M}$.

	Ring π -orbitals			Metal f-orbitals
Initial set(s) of C ₆ H ₆ -ring π -combinations (C ₆ -symmetry)	(4) $\times$ a ₁	(4) $\times$ e ₁	(4) $\times$ e ₂	
Total set of linear combinations resulting for T _d -symmetry	a ₁ t ₂	e t ₂	e t ₂	a ₁ t ₁ t ₂

and B_6^0 turned out negative with values of the ratio B_4^0/B_6^0 between $+8$ and $+1$ (with respect to the LLW-diagram this corresponds to x -values between -0.36 and -0.82) and thus admitting, if any, only the accidental degeneracy $E:T_2$ (see Fig. 2 and Table II). Anticipating, on the other hand, an ideal degeneracy $E:T_2$ for the f^2 -system, and considering $H_{ii}(5f)$ as unknown, a simple first-order CF-treatment of the isolated $^3\text{H}_4$ -manifold yields: $H_{ii}(5f) = -9.73$ eV. If, moreover, a simultaneous diagonalisation of the complete f^2 -configuration* is carried out with the condition that the sequence:

$$0 = E(E) = E(T_2) < E(T_1) < E(A_1) \dots$$

be verified, the correspondence of results shown in Table IV is obtained.

Table IV. The influence of J-mixing on the ratio B_4^0/B_6^0 , assuming ideal $E:T_2$ -degeneracy.

B_4^0 (given, in cm^{-1}) ≈ 0	—500	—750	—1000	—1500	
B_4^0/B_6^0 (calcd)	4.88	1.60	1.46	1.39	1.33

When these findings are translated back to the f^1 -case covered by the MHW-MO-formalism, $H_{ii}(5f)$ turns out to become increasingly more negative with decreasing B_4^0/B_6^0 . This trend is essentially due to the increasingly strong influence of J-mixing. *via* the CF, the complete neglect of which will yield $B_4^0/B_6^0 = 4.88$ (and provides the basis for the familiar LLW-diagrams).

* The spin-orbit coupling matrices and the CF-matrices of SATTEN *et al.*²⁹ have been used. The values of the spin-orbit coupling constant and of the Slater parameters adopted in the calculations, were the same as suggested by SATTEN *et al.*³⁰ for C₅₂ UCl₆.

In view of the rather low first ionisation potential of gaseous UCp₄ (6.5 ± 0.1 eV)³¹ it might be suggested that, as in the case of uranocene¹, electrons in some completely filled ligand orbitals have considerably higher energies than in incompletely filled 5f-metal orbitals. Rather similar cases have been deduced by JØRGENSEN²⁸ from the photoelectron spectra of numerous rare earth halide and oxide compounds but this phenomenon seems to be exhibited also by some d-metal acetylacetonates³².

5. Deviation from Pure Tetrahedral CF-Symmetry

Encouraged by the above results, we have also made an attempt to subject the real UCp₄-system to an appropriate AOM-treatment. Here, however, the large number of free parameters in the complete CF-Hamiltonian for S₄-symmetry (9) (in comparison with the five linearly independent equations yielding the CF-parameters within the framework of the AOM) requires several further simplifications.

$$\begin{aligned} \hat{H}_{CF}(S_4) = & B_2^0 \hat{Y}_2^0 + B_4^0 \hat{Y}_4^0 + B_4^4 (\hat{Y}_4^4 + \hat{Y}_4^{-4}) + \\ & B_6^0 \hat{Y}_6^0 + B_6^4 (\hat{Y}_6^4 + \hat{Y}_6^{-4}) + i \cdot B_4^{-4} (\hat{Y}_4^4 - \hat{Y}_4^{-4}) + \\ & i \cdot B_6^{-4} (\hat{Y}_6^4 - \hat{Y}_6^{-4}) \end{aligned} \quad (9)$$

In previous studies of S₄-systems the imaginary part of the complex CF-Hamiltonian has quite frequently been simply ignored³³⁻³⁷. This kind of truncation of $\hat{H}_{CF}(S_4)$ would formally correspond to a re-ascent from S₄- to D_{2d}-CF-symmetry.

It is, however, possible to eliminate one of the B_n^m by a rotation of the initial coordinate system about its z-axis by an angle $m\delta$ given by³⁸:

$$\tan(m\delta) = - (B_n^{-m}/B_n^m)^{1/2} \quad (10)$$

The new set of parameters B_n^m is thus related to the former one by:

$$\begin{aligned} B_n^m &= B_n^m \quad (m=0) \\ B_n^m &= [(B_n^m)^2 + (B_n^{-m})^2]^{1/2} \quad (m \neq 0) \end{aligned} \quad (11)$$

so that the full parameter set is reduced from virtually seven to six fully independent variables, whilst the point symmetry in question still remains S₄. Any further reduction of the set (for instance from six to five) is then only possible if for some pairs of parameters fixed ratios (*e.g.* $B_6^{-4}/B_6^4 = \text{const.}$) are introduced.

By adopting either the two latter simplifications or by neglecting the full imaginary part of $\hat{H}_{CF}(S_4)$ [of formula (9)], no more than five free variables B_n^m

will survive which, by the formalism of the AOM can again be transformed into linear combinations of the two AO-parameters e_σ and e_π only.

Accounting for the actual spatial positions⁴ of the twenty equivalent ring-C-atoms of the S₄-molecule UCp₄, but applying the truncated CF-Hamiltonian (*i.e.* going over to the effective CF-symmetry D_{2d}) the following set of linear combinations is obtained*:

$$\begin{aligned} B_2^0 &= -0.064 e_\sigma - 0.129 e_\pi \\ B_4^0 &= -0.222 e_\sigma - 0.118 e_\pi \\ B_6^0 &= -0.074 e_\sigma + 0.081 e_\pi \\ B_4^4 &= -1.407 e_\sigma - 0.609 e_\pi \\ B_6^4 &= +1.564 e_\sigma - 0.610 e_\pi \end{aligned} \quad (12)$$

The first-order energies of the CF-states derived from the ³H₄-manifold (classified in terms of D_{2d}-symmetry) are²¹:

$$\begin{aligned} E(A_1 I) &= 4D_2^0 + 16D_4^0 - 8D_6^0 - \\ &\frac{1}{2} \sqrt{(48D_2^0 - 4D_4^0 + 24D_6^0)^2 + [2\sqrt{2}(\sqrt{70}D_4^4 + 2\sqrt{70}D_6^4)]^2} \\ E(A_1 II) &= 4D_2^0 + 16D_4^0 - 8D_6^0 + \\ &\frac{1}{2} \sqrt{(48D_2^0 - 4D_4^0 + 24D_6^0)^2 + [2\sqrt{2}(\sqrt{70}D_4^4 + 2\sqrt{70}D_6^4)]^2} \\ E(A_2) &= 28D_2^0 + 14D_4^0 + 4D_6^0 \\ E(B_1) &= -8D_2^0 - 11D_4^0 + 22D_6^0 + 15D_4^4 - \\ &14D_6^4 \\ E(B_2) &= -8D_2^0 - 11D_4^0 + 22D_6^0 - 15D_4^4 + \\ &14D_6^4 \end{aligned} \quad (13)$$

$$\begin{aligned} E(E I) &= -5D_2^0 - 6D_4^0 - 8D_6^0 - \\ &\frac{1}{2} \sqrt{(24D_2^0 - 30D_4^0 - 18D_6^0)^2 + [2(5\sqrt{7}D_4^4 - \sqrt{7}D_6^4)]^2} \\ E(E II) &= -5D_2^0 - 6D_4^0 - 8D_6^0 + \\ &\frac{1}{2} \sqrt{(24D_2^0 - 30D_4^0 - 18D_6^0)^2 + [2(5\sqrt{7}D_4^4 - \sqrt{7}D_6^4)]^2} \end{aligned}$$

The quantities D_n^m occurring in (13) relate to the B_n^m -values as follows:

$$\begin{aligned} D_2^0 &= \alpha B_2^0 \quad D_4^0 = 60 \cdot \beta B_4^0 \quad D_6^0 = 1260 \cdot \gamma B_6^0 \\ D_4^4 &= 12 \cdot \beta B_4^4 \quad D_6^4 = 180 \cdot \gamma B_6^4 \end{aligned} \quad (14)$$

* The expressions presented by KUSE *et al.*³⁹ differ from those applied in this paper by one reversed phase factor.

Fig. 4. Angular overlap diagram of UCp₄ as obtained by neglecting the imaginary part of Eq. (9). The "tetrahedral" parent states are indicated on the left side of the diagram.

The corresponding AO-diagram resulting from the combination of (12) with (13) and (14) is shown in Fig. 4. It is seen from the diagram that the three essential conditions already deduced from the observed temperature dependence of the magnetic Sc of UCp₄, namely:

- i) a magnetically inactive (*i.e.* non-degenerate) CF-ground, state,
 - ii) non-vanishing NDE's with respect to the operator $\beta H(\hat{L} + 2\hat{S})$ between the CF-ground state and the first excited state,
 - iii) sufficiently low energies of the three (or at most four) lowest-lying CF-states to admit an appreciable thermal population at room temperature,
- are only verified within the range:
- $$0.33 < e_{\pi}/e_{\sigma} < 0.54.$$

The corresponding energetic sequence is:

$$E(A_{1I}) < E(E^I) < E(B_2) < E(B_1) < E(E^{II}) < E(A_2) < E(A_{1II}) \dots$$

The general appearance of the AO-diagram of the virtual D_{2d}-system shows a close resemblance to the AO-diagram of the T_d-model system (Fig. 3) confirming the initial idea of an essentially tetrahedral CF upon which weaker contributions of lower symmetry are superimposed.

Fairly similar AO-diagrams are also obtained if a CF of S₄-symmetry is maintained, provided that the ratio B₆⁻⁴/B₆⁴ adopts values between -0.25 and +0.25. In fact, numerous studies of rare earth systems involving S₄- or C_{3h}-symmetry (*i.e.* the CF-

Hamiltonian contains an imaginary term) have revealed that $B_n^m \gg B_n^{-m}$ ^{40, 41}. However, as a trivial consequence of the descent from D_{2d}- to S₄-symmetry, the crossover of the former D_{2d}-states B₁ and B₂ (which in S₄-symmetry both transform like B) will be avoided.

6. Tentative Simulation of the Observed Magnetic Data

As a common result of the various model considerations described in the preceding sections it has been found that the lowest-lying CF-states susceptible to thermal population can always be derived from the CF-states E and T₂ of a fictive tetrahedral molecule. This particular feature offers a useful starting point for an attempt to simulate the observed temperature dependence of the Sc of UCp₄.

Thus, it is assumed that the energetic order of the four parent tetrahedral CF-states be

$$E \approx T_2 < T_1 < A_1 \dots$$

The actual deviation of the CF-Hamiltonian from T_d-symmetry is essentially accounted for by admitting a weak additional perturbation in the sense of T_d → S₄. This is achieved by assuming the energetic order of the CF-states to be the same as in the AO-diagram for D_{2d}-symmetry within the range: $0.33 < e_{\pi}/e_{\sigma} < 0.54$ (see Fig. 4). On the other hand, the matrix elements of the magnetic field operator were determined using the unmodified tetrahedral eigenfunctions⁴² (for an appropriate correlation see Table V).

Table V. List of the eigenfunctions adopted, and of the "optimal" CF-energies obtained, in the simulation of the experimental Sc-data.

Rep. (T _d)	CF-Eigenfunction	Rep. (D _{2d})	Energy [cm ⁻¹]
E	$\sqrt{7/24} 4\rangle - \sqrt{5/12} 0\rangle + \sqrt{7/24} -4\rangle$	A _{1I}	0
	$\sqrt{1/2} 2\rangle + \sqrt{1/2} -2\rangle$	B ₁	250
T ₂	$\sqrt{7/8} 3\rangle - \sqrt{1/8} 1\rangle - \sqrt{7/8} -3\rangle + \sqrt{1/8} -1\rangle$	E ^I	20
	$\sqrt{1/2} 2\rangle - \sqrt{1/2} -2\rangle$	B ₂	190
T ₁	$-\sqrt{1/8} 3\rangle - \sqrt{7/8} 1\rangle + \sqrt{1/8} -3\rangle + \sqrt{7/8} -1\rangle$	E ^{II}	≈ 700
	$\sqrt{1/2} 4\rangle - \sqrt{1/2} -4\rangle$	A ₂	≈ 700
A ₁	$\sqrt{5/24} 4\rangle + \sqrt{7/12} 0\rangle + \sqrt{5/24} -4\rangle$	A _{1II}	> 2000

Ignoring, moreover, all contributions from the very high-lying singlet state A_1^{II} (in terms of D_{2d} -symmetry) the paramagnetic Sc is easily formulated by means of van Vleck's fundamental formula* (15)⁴³:

$$\chi = \frac{Q^2 N \sum_i [(W_i^I)^2/kT - 2 W_{ij}^{II}] \exp(-W_i^0/kT)}{\sum_i \exp(-W_i^0/kT)} \quad (15)$$

The quantities W_i^I and W_{ij}^{II} involve, as usual, the diagonal and non-diagonal matrix elements, respectively, of the magnetic field operator and are readily accessible from the wave functions given in Table V. As $W_0^0 = 0$, and $W_5^0 \approx W_4^0$, four different W_i^0 -values are considered as free parameters. An additional open variable is the quantity Q , which is intended to account for a reduction of all matrix elements by "higher order" effects such as J-mixing *via* the CF¹, reduction of the angular momentum caused by covalency effects⁴⁴ and deviation of the S_4 -CF-wave functions from the tetrahedral wave functions. N and k are the Loschmidt and Boltzmann constants, respectively.

It is possible to reproduce the two experimental curves (a) and (b) of Fig. 1 satisfactorily by the five W_i^0 -values listed in the right-hand column of Table V and one scaling factor $Q = 0.707$.

In the AO-diagram (Fig. 4) the relative spacing of these CF-energies is best accounted for if $e_\pi/e_\sigma = 0.50$, so that e_σ will formally amount to *ca.* 2000 cm⁻¹. It is quite remarkable that a good simulation of the experimental findings is achieved by only a single "scaling parameter" Q , although the actual value to be chosen is (as in the uranocene system¹) surprisingly low.

7. Concluding Remarks

It should be emphasized that the main purpose of the present study concerning the electronic structure of the $5f^2$ -system UCp₄ is to illuminate the usefulness, and individual limitations, of the simplest model conceptions available, rather than to reproduce the known properties of UCp₄ by very extended calculations. Thus, the strikingly successful simulation of the temperature dependence of χ as outlined in the preceding section can by no means serve as a "proof" of the CF-splitting

patterns developed on the basis of various simple theoretical approaches. There is, nevertheless, a sufficiently large amount of mutual consistency between the statements deduced from the experimental facts, both directly and *via* the semi-empirical approaches, that future refinements could hopefully make use of at least some of the present results.

On the other hand, comparing the present treatment of UCp₄ with a previous study of the likewise organometallic "uranocene" system $(\eta^8\text{-C}_8\text{H}_8)_2\text{U(IV)}$ ¹, it is seen that only in the UCp₄-case both the purely electrostatic approach (EPC), and the alternative models which take account of covalent interactions (AOM *viz.* MHW-MO), lead to essentially the same results. Since both electrostatic and covalent interactions will undoubtedly determine the actual CF-splitting pattern (and, of course, the underlying parameters), the treatment of UCp₄ suffers from less ambiguity than the study of $\text{U(C}_8\text{H}_8)_2$.

Another point of interest is that both treatments tend to favour situations in which the one-electron energy of the unperturbed $5f$ -orbitals is assumed to be somewhat lower than the energies of those orbitals of the respective cyclic π -systems which turn out to be most relevant for the formation of the complexes (*i.e.* the linear combinations transforming as e_1 and e_2 in C_5 - and C_8 -symmetry, respectively). Although this particular energetic order of starting orbitals would be consistent with a number of recent photoelectron spectroscopic results, this feature of the derived electronic structure of the complexes might lead to some controversy in that some completely occupied ligand orbitals would be of higher energy than the partly filled "5f-like" orbitals.

MÜLLER has shown that the first ionisation potential (=I.P.) of numerous complexes of the type $\text{Cp}_3\text{Ln(III)}$ ($\text{Ln} = \text{Pr, Ho, Tm, Yb and Lu}$) are quite distinctly centred around 7.5 eV³¹. The absence of any variation of the data which parallel the known redox potentials of the Ln(III) -systems suggests that here ionisation takes always place from a distinct "ligand-like" orbital. Consequently, the observed first I.P. of the complex $\text{Cp}_3\text{U(IV)F}$ (7.53 eV) should be assigned to a corresponding mode of ligand ionisation in the $\text{Cp}_3\text{Ln(III)}$ -systems. Adopting Jørgensen's arguments concerning the intramolecular (ligand) electron repul-

* Here the application of VAN VLECK's formula is justified, even at very low temperatures, because UCp₄ has a non-magnetic CF-ground state.

sion in the complexes with crowded η^5 -C₅H₅-ligands⁴⁵, a substantial lowering of the first I. P. is expected and in fact observed when the fluoride ligand is substituted by another η^5 -C₅H₅-ring (I. P. of UCp₄ = 6.5 eV)*. Therefore for UCp₄ it seems not unreasonable to assume the initially introduced starting condition: $E(5f) < E(e_1, \text{ring})$.

It is finally worth mentioning that the sign of the "optimal" AO-parameters e_σ and e_π turn out negative for U(C₈H₈)₂ but positive for UCp₄, whilst the three CF-parameters B_n^0 ($n = 2, 4, 6$) are in both cases negative. The main reason for this sign reversal of the e_λ -values is that the AOM-treatment has been carried out by accounting for no more than two singular variables e_σ and e_π , although the π -interaction within each of the cyclic ligand systems is undoubtedly too large to be simply neglected. Hence, each of the "optimal" e_λ ($\lambda = \sigma$ and π)-values is necessarily understood as an appropriate average value over three *viz.* four individual $e_{\lambda j}$ -values, where each j label denotes one of the

different linear combinations of ligand π -orbitals. The main justification for considering the AOM as a still useful semiempirical tool is provided by the rather close similarity of all possible ratios $e_{\pi j}/e_{\sigma j}$. By inspection of the corresponding group overlap integrals $G^j = G^j(S_\sigma) + G^j(S_\pi)$ it is easily verified that the individual ratios $e_{\pi j}/e_{\sigma j}$ all adopt very similar values, which moreover, all lie within the range: $-1 < e_{\pi j}/e_{\sigma j} < 1$. Fairly similar conditions should therefore hold for the two average values e_σ and e_π too, thus offering the application of appropriate diagrams as outlined in section 5.

For any extension of this work additional information is undoubtedly needed from other experimental sources and will hopefully be provided in the near future by low-temperature electronic f-f-absorption spectra in the near infrared and visible regions.

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* Quite similarly, the transition from the complex Cp₃Yb(III) to the (monomeric) species Cp₂Yb(III)Cl corresponds to a substantial increase of the first I. P. (from 7.30 to 8.65 eV³¹).

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