Electronic Structure of the Principal Uranium Centre in Alkali Fluorides

W. A. Runciman,^A B. Srinivasan,^{A, B} and S. Saebo^{C, D}

^A Department of Solid State Physics, Research School of Physical Sciences, Australian National University, G.P.O. Box 4, Canberra, A.C.T. 2601.

^B Present address: D1-119 Bonn Avenue, IIT Madras 600036, India.

^C Research School of Chemistry, Australian National University,

G.P.O. Box 4, Canberra, A.C.T. 2601.

^D Present address: Department of Chemistry,

Mississippi State University, MS 39762, U.S.A.

Abstract

Fluorescent centres are formed when hexavalent uranium is incorporated into lithium fluoride and sodium fluoride in an oxygen atmosphere. The principal centre is believed to consist of a UO_5F group. Calculations have been made of the electronic structure of this centre assuming that the excited states are due to charge transfer transitions. Different models are considered and fitting procedures used to find parameters yielding good agreement with the energy levels and g values of the seven lowest excited states of the centre in sodium fluoride. A similar model is believed to be applicable to the principal centre in lithium fluoride.

1. Introduction

Uranium-doped crystals of lithium fluoride and sodium fluoride grown in an oxygen atmosphere have complex spectra both in absorption and emission (Runciman et al. 1981). Polarised excitation using tunable dye lasers provides high resolution spectra giving information on the symmetry of the fluorescent centres (Srinivasan et al. 1985). These fluorescent centres are not obtained in the absence of oxygen. Impurities can affect the fluorescent centres and recent progress has been made on this very complex problem (Lupei et al. 1985). In the absence of impurities the principal centre has tetragonal symmetry, point group C_{4v} , and is believed to consist of a UO₅F group (see Fig. 1). On an ionic model the U^{6+} ion substitutes for an M^+ alkali ion and five O^{2-} ions substitute for five of the six nearest neighbour F^{-} ions (Feofilov 1959). It is expected that these and neighbouring ions will relax to positions of minimum energy while maintaining the C_{4v} point group symmetry found experimentally (Runciman et al. 1985). This centre satisfies the requirements of localised charge compensation (Runciman 1955). The purpose of the present work is to find a theoretical explanation for the energy levels and g values found for the seven lowest excited states of NaF: U, O (see Fig. 2). The summary of the results which has already appeared (Runciman et al. 1984) erroneously recorded a g value of 0.45 for the 3E level instead of 0.46 for the 2E level. The q value for the 3E level is small and has not been measured. The experimental energy levels for LiF: U, O are similar to those for NaF: U, O and about 1200 cm⁻¹ higher in energy above the ground state. However, there is some uncertainty about a missing level believed to be near 24200 cm⁻¹ (Srinivasan *et al.*



Fig. 2. Experimental energy levels (in units of cm^{-1}) and g values for the principal centre in NaF: U, O, compared with the theoretical values calculated on the basis of the b₂ f excited configuration using the final values of the variables in Table 6.

1985) and so we preferred to carry out the detailed fitting on the principal centre of NaF: U, O. By analogy with the linear uranyl group $UO_2^{2^+}$ (Denning *et al.* 1979) and the octahedral uranate group $UO_6^{6^-}$ (Bleijenberg 1980), the excited states are attributed to charge transfer transitions in which an electron from the bonding oxygen ions transfers into an empty 5f orbital of the uranium ion. The ground state is assumed to be an A_1 state as the U^{6+} and O^{2-} ions have closed shell configurations, and covalent mixing will not produce a state of different symmetry at lower energy. Either the axial oxygen ion or the equatorial oxygen ions can be the source of the ligand 2p oxygen orbital acting as the donor orbital. In either case the orbital may be the $\sigma(m_i=0)$ orbital or the $\pi(m_i=\pm 1)$ orbital. In the case of an electron being removed from the σ orbital the excited configuration contains an incomplete σ shell Electronic Structure of Principal Uranium Centre

with one occupied orbital and is denoted by σf . However, when a π electron is transferred there remains an incomplete shell with three filled orbitals, and the excited configuration is denoted by $\pi^3 f$. When considering the equatorial oxygen orbitals it is necessary to take linear combinations transforming as representations of the $C_{4\nu}$ point group. All the f orbitals, σ , π , δ , and ϕ , are included in the excited configurations. Similar to other surrounding ions, the fluorine ion in the UO₅F group is expected to remain unchanged and is not included in the detailed calculations.

The calculations reported here are part of a wider investigation of uranium-oxygen complexes (Srinivasan 1982). In a parallel investigation the formation energy of clusters of point defects has been calculated on an ionic model (Runciman *et al.* 1985). The results are relevant to deciding the energetically favourable configuration for complex clusters such as U_2O_{10} , which may be regarded as a dimer of the UO_5 group considered here.

2. Hamiltonian and the Energy Matrices

The Hamiltonian has contributions from the electrons in the incomplete σ or π oxygen orbitals and in the 5f uranium orbital and can be written as

$$H = \sum_{i} (H_{\rm el} + H_{\rm cf} + H_{\rm so})_{i} + \sum_{i,j,\ i < j} e^{2} / r_{ij},$$

where $H_{\rm el}$ is the one-electron term, $H_{\rm cf}$ is the crystal field term, $H_{\rm so}$ is the spin-orbit term and e^2/r_{ij} is the electron-electron repulsion term. Smaller interactions such as the spin-spin interaction are neglected.

For the uranyl ion, construction of the basis states can be made using either $\Lambda - \Sigma$ or $\omega - \omega$ coupling schemes (Denning *et al.* 1979). The former is preferable when the electron-electron repulsion predominates over the spin-orbit coupling and the latter when the reverse is true. Since neither interaction is dominant the choice is largely irrelevant as complete matrices have to be diagonalised. The $\omega - \omega$ scheme was used in the present calculation, and then basis states were found with the appropriate transformation properties with regard to the rotation and mirror operations of C_{4v} . The representations of C_{4v} are A_1 , A_2 , B_1 , B_2 and E.

There are eleven configurations of the excited states to be considered. The axial configurations are σf and $\pi^3 f$. The equatorial σf configurations are $a_1 f$, $b_1 f$ and $e^{3}f$. The equatorial models involving $2p_{z}$ orbitals are $a_{1}f$, $b_{1}f$ and $e^{3}f$, while those involving $2p_x$ and $2p_y$ orbitals are $a_2 f$, $b_2 f$ and $e^3 f$. Since the best fit was obtained for the b₂ f model the basis states for this configuration in a crystal field of C_{4v} symmetry are listed in Table 1. Values of g_{\parallel} for the Zeeman effect with the magnetic field parallel to the major axis of the centre are listed for the E states and are simply the expectation values of $L_z + 2S_z$. The transverse Zeeman effect has $g_{\perp} = 0$ for all states. Only the E^+ basis states are listed as, in the absence of a magnetic field, the E^- states have energies identical to those of the E^+ states. The b₂ orbital has the form $\frac{1}{2}(y_1 + x_2 - y_3 - x_4)$ where, for instance, y_1 is the $2p_v$ orbital on oxygen ion 1 (see Fig. 1). It would be helpful if there was a clear a priori indication whether the electron is donated by the equatorial ions O_{1-4} or the axial oxygen ion O_5 . It is likely that the U-F distance is greater than the U-O distances on account of the smaller electrostatic attraction, but conjectures on the relative interionic distances for the different U-O bonds are less reliable.

Represen- tation	State	Wavefunction	Represen- tation	State	Wavefunction	g_{\parallel}
$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$	φ ₁ φ ₂ φ ₃ φ ₄	$\begin{array}{c} \sqrt{\frac{1}{2}} (1b_2 2\pi^+ (\pm) 1\bar{b}_2 2\bar{\pi}^-) \\ \sqrt{\frac{1}{2}} (1b_2 2\bar{\delta}^- (\pm) 1\bar{b}_2 2\bar{\delta}^+) \\ \sqrt{\frac{1}{2}} (1b_2 2\bar{\delta}^+ (\pm) 1\bar{b}_2 2\bar{\delta}^-) \\ \sqrt{\frac{1}{2}} (1b_2 2\bar{\phi}^- (\pm) 1\bar{b}_2 2\bar{\phi}^+) \end{array}$	Е	φ ₁ φ ₂ φ ₃ φ ₄	$ \begin{array}{c} 1b_{2} 2\sigma \\ 1\bar{b}_{2} 2\pi^{+} \\ 1b_{2} 2\bar{\pi}^{+} \\ 1\bar{b}_{2} 2\bar{\delta}^{+} \\ 1\bar{b}_{2} 2\bar{\delta}^{+} \end{array} $	2 1 1 0
$\binom{B_1}{B_2}$	Φ1 Φ2 Φ3	$ \begin{array}{l} \sqrt{\frac{1}{2}}(1b_2 2\bar{\sigma} (\pm) 1\bar{b}_2 2\sigma) \\ \sqrt{\frac{1}{2}}(1b_2 2\pi^- (\pm) 1\bar{b}_2 2\bar{\pi}^+) \\ \sqrt{\frac{1}{2}}(1b_2 2\phi^+ (\pm) 1\bar{b}_2 2\bar{\phi}^-) \end{array} $		Φ5 Φ6 Φ7	$ 1b_2 2\delta^- $ $ 1\bar{b}_2 2\bar{\phi}^- $ $ 1b_2 2\bar{\phi}^- $	-4 - 3 - 3

 Table 1.
 Basis states for the equatorial b₂ f model*

* Here and in Tables 2 and 3 the upper (and lower) signs in parentheses correspond to the upper A_1 or B_1 (and lower A_2 or B_2) representations respectively.

The matrix elements for the one-electron interactions were expressed in terms of commonly used parameters using formulae for the crystal field (Wybourne 1965) and spin-orbit (Griffith 1961) interactions. Similarly, the electron-electron interaction terms were expressed in terms of the standard integrals by standard molecular orbital procedures (Richards and Horsley 1970). Raftery and co-workers (Raftery *et al.* 1972; Scott *et al.* 1973) have obtained the Coulomb and exchange integrals between the molecular orbitals for various simple electron configurations of linear molecules. These were used, when appropriate, to check the validity of the matrix elements of e^2/r_{12} calculated in the present work. The matrices derived in this way for the b₂ f configuration are shown in Table 2. Terms in the diagonal elements of the matrices are grouped together and given a single label α_{b_2j} , where $j = \sigma$, π , δ or ϕ , for convenience in presenting the matrix elements in tabular form. The α_{b_2j} symbols in Table 2 are defined as follows:

$$\begin{split} \alpha_{\mathbf{b}_{2}\sigma} &= \epsilon_{1\mathbf{b}_{2}} + \epsilon_{2\sigma} + \frac{4}{15}B_{0}^{2} + \frac{2}{11}B_{0}^{4} + \frac{100}{429}B_{0}^{6} + J_{1\mathbf{b}_{2}2\sigma} \,, \\ \alpha_{\mathbf{b}_{2}\pi} &= \epsilon_{1\mathbf{b}_{2}} + \epsilon_{2\pi} + \frac{1}{5}B_{0}^{2} + \frac{1}{33}B_{0}^{4} - \frac{25}{143}B_{0}^{6} + J_{1\mathbf{b}_{2}2\pi} \,, \\ \alpha_{\mathbf{b}_{2}\delta} &= \epsilon_{1\mathbf{b}_{2}} + \epsilon_{2\delta} - \frac{7}{33}B_{0}^{4} + \frac{10}{143}B_{0}^{6} + J_{1\mathbf{b}_{2}2\delta} \,, \\ \alpha_{\mathbf{b}_{2}\phi} &= \epsilon_{1\mathbf{b}_{2}} + \epsilon_{2\phi} - \frac{1}{3}B_{0}^{2} + \frac{1}{11}B_{0}^{4} - \frac{5}{429}B_{0}^{6} + J_{1\mathbf{b}_{2}2\phi} \,. \end{split}$$

Since the matrices are symmetric only elements on or above the diagonal are listed. Matrices for the $a_2 f$, $b_1 f$ and $a_1 f$ configurations are obtained by interchanging respectively the a and b labels, the 1 and 2 subscripts or both.

The basis states for the $\pi^3 f$ configuration in a crystal field of $C_{4\nu}$ symmetry are listed in Table 3. Those for the $e^3 f$ configuration are simply obtained by the appropriate substitution of e for π throughout. The g_{\parallel} values for the E states are listed for both the $\pi^3 f$ and $e^3 f$ configurations.[†]

[†] Copies of the matrices for the π^3 f configuration are available on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 314 Albert Street, East Melbourne, Vic. 3002, Australia.

	Tahl	e 2. Matrix	elements of excite	d states for the $b_2 f$ config $/A$.	uration	
			(a) Excited state	symmetry $\begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$		
	φ1		ϕ_2	φ3	ф	4
φ1	$a_{b_2\pi} - K_{1b_22}$	$\pi + \frac{1}{2} \zeta_{u}$	0	$\frac{\sqrt{10}}{2}\xi_{\rm u}$	$\frac{\sqrt{42}}{33}B_4^4-$	$\frac{5\sqrt{210}}{429}B_4^6$
φ2			$a_{b_2\delta} + \xi_u$	$\frac{\sqrt{70}}{33}B_4^4 + \frac{10\sqrt{14}}{143}B_4^{6}(\mp)$	$\frac{\sqrt{6}}{2}$	5 - ¢u
φ3				$\alpha_{b_2\delta} - \zeta_u$, ,
φ4				· .	$a_{b_2\phi} - K_1$	$b_2 2\phi - \frac{2}{2} \xi_u$
			(b) Excited state	symmetry $\begin{pmatrix} B_1 \\ B_2 \end{pmatrix}$		
		ф 	1	φ2	φ3	
	φ ₁	$a_{b_2\sigma}(\mp)$	$(K_{1b_22\sigma})$	$\sqrt{3} \xi_u$	0	
	ϕ_2		α ^ρ	$_2\pi - K_{1b_22\pi} - \frac{1}{2}\zeta_{\mathrm{u}}$	$\frac{V42}{33}B_4^4 - \frac{5V210}{429}B_4^6$	
	φ ₃				$\alpha{b_2\phi} - K_{1b_22\sigma} - \frac{3}{2}\xi_u$	
	-		(c) Excited sta	tte symmetry E		
φ1	ϕ_2	ф3	φ4	φ5	ϕ_6	φ7
$a_{b,\sigma} - K_{1b,2\sigma}$	0	$\sqrt{3}\xi_{\rm u}$	0	0	0	0
4	$a_{b,\pi}+\frac{1}{2}\zeta_{u}$	$-K_{1b,2\pi}$	$\frac{\sqrt{10}}{2}\xi_{\rm u}$	0	${\sqrt{42}\over 32} B_4^4 - {5\sqrt{210}\over 470} B_4^6$	0
	, σ	$\frac{1}{h} = -\frac{1}{3}\zeta_{11}$	7 0	0	0	$\frac{\sqrt{42}}{22}B_4^4 - \frac{5\sqrt{210}}{100}B_4$
			$a_{h,\delta} - K_{l,h,2\delta} - \zeta_u$	$\frac{\sqrt{70}}{22} B_4^4 + \frac{10\sqrt{14}}{12} B_4^6$	0	0 0
				$a_{h,s} - K_{1h,2s} + \xi_{11}$	<u></u>	0
					$\frac{2}{\alpha_{b_2\phi}-\frac{3}{2}\xi_u}$	$-K_{1{ m b}_22{ m \phi}}$
						$a_{b_2\phi}+\frac{3}{2}\xi_u$

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559

6

-4 0

-2

5

1

- 5

-1

		Table 3. Basis states for the π^{3} f model		
Represen- tation	State	Wavefunction	g_{\parallel}	$g_{\parallel}(e^{3}f)$
$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$	φ ₁ φ ₂ φ ₃ φ ₄ φ ₅ φ ₆	$ \begin{array}{c} \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\bar{\pi}^{-}1\bar{\pi}^{+}2\bar{\sigma} (\pm) 1\bar{\pi}^{-}1\pi^{+}1\pi^{-}2\sigma \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\bar{\pi}^{-}1\bar{\pi}^{+}2\pi^{-} (\pm) 1\bar{\pi}^{-}1\pi^{+}1\pi^{-}2\bar{\pi}^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{+}2\bar{\pi}^{-} (\pm) 1\bar{\pi}^{-}1\bar{\pi}^{+}1\pi^{-}2\pi^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{+}2\delta^{+} (\pm) 1\bar{\pi}^{-}1\bar{\pi}^{+}1\pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{+}2\delta^{-} (\pm) 1\bar{\pi}^{-}1\bar{\pi}^{+}1\pi^{-}2\bar{\delta}^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\bar{\pi}^{-}1\bar{\pi}^{+}2\bar{\delta}^{+} (\pm) 1\bar{\pi}^{-}1\pi^{+}1\pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{+}2\bar{\delta}^{+} (\pm) 1\bar{\pi}^{-}1\pi^{+}1\pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{+}2\bar{\delta}^{+} (\pm) 1\bar{\pi}^{-}1\bar{\pi}^{+}1\pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{-}2\bar{\delta}^{+} (\pm) 1\bar{\pi}^{-}1\bar{\pi}^{+}1\pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{-}2\bar{\delta}^{+} (\pm) 1\bar{\pi}^{-}1\bar{\pi}^{+}1\pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\pi}^{-}2\bar{\delta}^{+} (\pm) 1\bar{\delta}^{-}1\bar{\delta}^{+} \pi^{-}2\bar{\delta}^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\delta}^{-}1\bar{\delta}^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\delta}^{-}1\bar{\delta}^{+}1\bar{\delta}^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\delta}^{-}1\bar{\delta}^{+}1\bar{\delta}^{+}1\bar{\delta}^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+}1\pi^{-}1\bar{\delta}^{-}1\bar{\delta}^{+}1$		
$\begin{pmatrix} B_1 \\ B_2 \end{pmatrix}$	Ψ7 Φ1 Φ2 Φ3 Φ4 Φ5 Φ6 Φ7	$ \begin{array}{c} \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{+} 2\phi^{+} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\phi^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{+} 2\sigma (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\sigma^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{+} 2\pi^{+} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\pi^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{+} 2\bar{\kappa}^{+} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\pi^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{-} 2\delta^{+} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\delta^{-} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{-} 2\delta^{+} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\delta^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{+} 2\phi^{-} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\phi^{+} \right\} \\ \sqrt{\frac{1}{2}} \left\{ 1\pi^{+} 1\pi^{-} 1\pi^{+} 2\phi^{-} (\pm) 1\pi^{-} 1\pi^{+} 1\pi^{-} 2\phi^{+} \right\} \end{array} $		
Е	φ ₁	$ 1\pi^+1\pi^-1\pi^+2\sigma $ $ 1\pi^+1\pi^-1\pi^+2\sigma $	1	0
	Ψ2 Φ3 Φ4 Φ5 Φ6 Φ7 Φ8 Φ9	$\begin{vmatrix} 1\pi & 1\pi & 25 \\ 1\pi + 1\bar{\pi} - 1\bar{\pi} + 2\bar{\pi} + \\ 1\pi + 1\pi - 1\bar{\pi} + 2\pi - \\ 1\pi + 1\pi - 1\bar{\pi} - 2\pi + \\ 1\bar{\pi} + 1\pi - 1\bar{\pi} - 2\bar{\pi} - \\ 1\pi + 1\pi - 1\bar{\pi} - 2\bar{\delta} - \\ 1\pi + 1\pi - 1\bar{\pi} - 2\bar{\delta} - \\ 1\bar{\pi} + 1\pi - 1\bar{\pi} - 2\bar{\delta} - \end{vmatrix}$	$ \begin{array}{c} 1 \\ 0 \\ 2 \\ -4 \\ 1 \\ -3 \\ \end{array} $	-1 1 -3 2 -2
	Φ 10	$ 1\pi^+ 1\pi^- 1\bar{\pi}^- 2\bar{\delta}^- $	<u> </u>	-2

3. Results

φ11

ф₁₂

φ13

 ϕ_{14}

Values of the parameters had to be estimated as a starting point for a least-squares fit of the theoretical to the experimental energy levels and g values. The spin-orbit coupling constant for the uranium ion ζ_u was taken to be 1950 cm⁻¹, a value within the range found for the uranyl molecule (Denning et al. 1979). When needed a value between 700 and 1000 cm^{-1} was used for the spin-orbit coupling constant for the oxygen orbital. Crystal field parameters were estimated from earlier analyses such as the study of U^{5+} centres in irradiated LiF: U, O crystals (Parrot *et al.* 1977). The parameters chosen indicate that the crystal field is strong relative to spin-orbit coupling (Edelstein et al. 1974).

 $|1\pi^+1\pi^-1\pi^+2\phi^+$

 $\begin{array}{c} 1\pi & 1\pi & 2\bar{\Phi} \\ 1\pi + 1\bar{\pi} - 1\bar{\pi} + 2\bar{\Phi} \\ 1\bar{\pi} + 1\pi - 1\bar{\pi} - 2\bar{\Phi} \end{array}$

 $|1\pi^+1\pi^-1\pi^+2\phi^-|$

The computer program system MOLECULE (Almløf 1974), which provides empirical calculations of the electronic structure of molecules, was used to find the two-electron integrals. In this program, which uses cartesian gaussians, the basis set used is made up of fixed linear combinations of gaussian-type functions:

$$\chi_j = \sum_p d_{pj} \phi_p,$$

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where

$$\phi_p = N_p (x - x_p)^{l_p} (y - y_p)^{m_p} (z - z_p)^{n_p} \exp\{-\alpha_p (r - r_p)^2\},$$

with the normalisation constant

$$N_p = \left\{ \left(\frac{2\alpha_p}{\pi}\right)^{\frac{3}{2}} \frac{(4\alpha_p)^{l_p + m_p + n_p}}{(2l_p - 1)!! (2m_p - 1)!! (2n_p - 1)!!} \right\}^{\frac{1}{2}}$$

where (2l-1)!! = 1.3.5...2l-1 and where $l_p + m_p + n_p = l$, the orbital angular momentum.

Table -	4.	Atomic	basis	sets
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Exponent	Contraction coefficient
Oxyget	n 2p function
0.075139	0.391957
0.231031	0.607684
0.994203	0.155916
Uraniur	n 5f function
0.30736	0.28834
1.05332	0.46846
3.10915	0.32932
9.43646	0.07457



Fig. 3. Amplitude $P_{nl}(r) = rR_{nl}(r)$ of the uranium 5f orbital (solid curve) and the oxygen 2p orbital (dashed curve).

The radial wavefunction for the uranium 5f orbital was a linear combination (contraction) of four gaussian functions (Kahn *et al.* 1978), and for the oxygen 2p orbital a linear combination of three gaussian functions (Hehre *et al.* 1969). Exponents and contraction coefficients are given in Table 4, and Fig. 3 shows the amplitudes of the uranium 5f orbital and oxygen 2p orbital given by these basis sets. The radial node is not reproduced by this 5f wavefunction, but this is not significant as the fit to the numerical wavefunction is good in the region of high electron density. The

Oxyge	en 2p functions	Ura	nium 5f functions
1σ	$\frac{\sqrt{3}}{2\sqrt{\pi}}\frac{z}{r}$	2σ	$\frac{\sqrt{7}}{2\sqrt{\pi} r^3} (z^3 - \frac{3}{2}zx^2 - \frac{3}{2}zy^2)$
$1\pi^{\pm}$	$\mp \frac{\sqrt{3}}{2(2\pi)^{\frac{1}{2}}} \frac{x \pm iy}{r}$	$2\pi^{\pm}$	$\mp \frac{\sqrt{21}}{4\sqrt{\pi} r^3} (2z^2 - \frac{1}{2}x^2 - \frac{1}{2}y^2) (x \pm iy)$
	- < /	$2\delta^{\pm}$	$\frac{\sqrt{105}}{2(2\pi)^{\frac{1}{2}}r^3}(\frac{1}{2}zx^2 - \frac{1}{2}zy^2 \pm ixyz)$
		$2\phi^{\pm}$	$\mp \frac{\sqrt{35}}{8\sqrt{\pi} r^3} \{ (x^3 - 3xy^2) \pm i(3x^2y - y^3) \}$

Table 5. Explicit forms of angular wavefunctions in cartesian coordinates (Ballhausen 1962)

Table 6. Initial and final parameters for the b_2 f fit (in units of cm⁻¹)

Variable	Initial value	Final value	Variable	Initial value	Final value
$K_{b_2\sigma} K_{b_2\pi} K_{b_2\delta} K_{b_2\phi}$	266 414 402 1604	835 1741 3023 5545	$\begin{array}{c}a_{b_2\sigma}-a_{b_2\pi}\\a_{b_2\delta}-a_{b_2\pi}\\a_{b_2\phi}-a_{b_2\pi}\\B_4^4\\B_4^6\\B_4^6\end{array}$	7000 3000 5000 13000 8000	440 3600 3656 6798 6700

oxygen orbital contains a radial scaling factor which was about 2.25 in the molecular calculations of Hehre et al. (1969). The 2p orbital is expected to be diffuse for a doubly negative ion in a solid and a scaling factor of about 0.59 has been used. The explicit normalised forms of the angular wavefunctions used are given in Table 5; these follow the phase convention used by Griffith (1961). The interionic distance was chosen to be 1.7 Å, a value appropriate for the uranyl ion. This is likely to be a lower limit for the UO_5F group. The required exchange integrals are linear combinations of the cartesian contributions calculated using MOLECULE and the results are given in Table 6. Naturally, calculations at larger interionic distances yielded smaller values of the Coulomb and exchange integrals. The differences of the one-electron energies of the σ , δ and ϕ orbitals relative to the π orbital and the crystal field parameters were chosen by reference to earlier calculations. The precise values were not regarded as critical as these parameters were allowed to vary to obtain a least-squares fit. Programs from the ANU Computer Library ANULIB* EIGEN and ANULIB* PRAXIS were used for the eigenvalue and least-squares calculations; the procedure is described in more detail elsewhere (Srinivasan 1982). Solutions for different configurations were rejected if they produced lowest excited A₁, B₁, B₂ or E states. The $\pi^3 f$ and $e^3 f$ models produced too many low lying levels for a fit to be obtained. It proved to be surprisingly difficult to obtain a fit to the experimental levels and g values by varying the one-electron energy differences and the crystal field parameters. The exchange integrals were then allowed to vary (see Table 6) and a reasonable fit was obtained for the b_2 f configuration as shown in Fig. 2. Similar results are expected for lithium fluoride, but no fitting was attempted in view of the additional uncertainty in the energy level scheme mentioned earlier.

4. Discussion

In the light of the unexpectedly large values for the exchange integrals it is reasonable to ask whether there is likely to be an alternative solution to the energy level calculation. There is likely to be configuration mixing, but this might be expected to be greatest between orbitals of the same symmetry. In the eleven configurations considered there is only one b_2 orbital so this case is unaltered. By mixing σf with the two $a_1 f$ configurations the character of the solutions will not be altered. In particular it is difficult to get a low g value for the lowest excited state while obtaining the separation of the lowest E state above the A_2 and A_1 states.

It is tempting to conjecture that the lowest A_2 , A_1 and E levels are components of a ³E group of levels split by a spin-orbit interaction. In this case we would expect B_1 and B_2 levels about as high above the E level as the E level is above the A_1 and A_2 levels.

There is a possibility that there are missing A_1 , A_2 and E levels of very low oscillator strength which have remained undetected, and considerable effort has been made with no avail to find other levels. The lowest A_2 level is readily detected by fluorescence and appears weakly in absorption as the transition has a magnetic dipole character. The higher A_2 levels will be difficult to detect. Transitions to B_1 and B_2 levels are forbidden, but it can be assumed that there are no such levels just below the A_2 level as this would alter the fluorescence lifetime at low temperatures in a manner which is not observed.

An attempt was made to locate B_1 and B_2 states by applying uniaxial stress in laser excitation experiments. The B_1 and B_2 transitions forbidden in C_{4v} symmetry become allowed A_1 transitions in C_{2v} symmetry when stress is applied along [100] and [110] directions respectively. No new lines were observed in the excitation spectra with stresses applied to the crystal samples up to 10 kg mm⁻².

If more energy levels are found it could affect the analysis significantly and in particular it could require further consideration of the $\pi^3 f$ and $e^3 f$ models. In particular, it may be useful to adopt a strong crystal field model. In a cubic field the f orbitals will have a_{2u} lowest and for large crystal fields the t_{2u} orbitals are at lower energy than the t_{1u} orbitals (Lea *et al.* 1962). Calculations indicate that this is the case for the UF₆ molecule (Boring and Wood 1979*a*, 1979*b*). It is an attractive feature of an $e^3 f$ model that the lowest E state would arise from $e^3 a_2$ which has g = 0. The difficulty is that there should be two low lying E levels arising from ³E and ¹E. Presumably the transition to the E level arising from ³E will have a lesser intensity than that to the ¹E level and it may be that the former is too weak to be observed.

Many aspects of the electronic structure of UO_5F groups remain to be established. Experimentally, more information may be obtained using two-photon absorption. This is the first detailed calculation of the energy levels of the UO_5F complex, and the agreement found with experiment is encouraging considering the simplicity of the approach used. Theoretically more elaborate relativistic calculations are required along the lines of those carried out for the octahedral UF_6 molecule (Boring and Wood 1979*a*, 1979*b*; Hay *et al.* 1979; Hay 1983). It may be revealing to study octahedral UO_6 complexes, as found in uranates such as Ba_2CaUO_6 (Steward and Runciman 1953).

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Guest Comment

This issue contains the papers associated with a highly successful workshop held at Strathgordon, Tasmania, 3–7 February 1986, to define the state of the art for both experimental and theoretical studies on problems related to the characterisation of excited and ionised states of atoms and molecules. The meeting addressed a number of the outstanding problems which remain to be solved, and explored areas where fruitful joint research projects between Australian and American scientists could be either initiated, or where existing collaborations could be strengthened. Discussions were relevant to many unanswered questions in basic physics, chemistry and astrophysics, as well as a wide range of technological applications including advances in high energy laser systems, plasmas for new energy sources and computer oriented studies.

The meeting was held under the USA–Australia Bilateral Science and Technology Agreement with financial support provided by the Australian Government through the Department of Science, and by the American Government through the National Science Foundation.

Topics addressed during the workshop included a comparison of synchrotron radiation and electron impact methods for probing electronic structure; the importance of relativistic effects in atomic and molecular calculations; quantum methods for the calculation of accurate wavefunctions for molecular ions with emphasis on correlation, *ab initio* and many-body perturbation methods; future directions for photoelectron spectroscopy, cross sections and angular resolved measurements for both atoms and molecules; and lifetime studies and secondary X-ray and Auger electron emission processes.

The workshop provided a venue to enable scientists from both countries to identify areas of mutual expertise and to appreciate the scientific achievements and resources available for co-operative research. The meeting reinforced the great value of close interaction between theorists and experimentalists in this field. This feature is evident from consideration of the papers contained in this issue. In some areas of chemical physics it is clear that Australia does not have the financial resources to independently undertake major experiments involving expensive equipment. However, the potential for collaborative research with our American colleagues and scientists from other nations is clearly very good. Furthermore, theoretical work being undertaken in Australia is providing the basis for understanding complex experiments that are performed elsewhere. The continuation of scientific workshops and international exchanges of scientists is essential to maintain the vitality of Australian science.

F. P. Larkins University of Tasmania May 1986

