Inorg. Chem. **1994,** *33,* 2315-2316 **2315**

Theoretical Investigation of the Effects of Spin-Orbit Coupling on the Valence Photoelectron Spectrum of OsO_4

Bruce E. Bursten,[†] Jennifer C. Green,*[,‡] and Nikolas Kaltsoyannis[†,‡]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Inorganic Chemistry Laboratory,
University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

Received July 2, 1993

The structural simplicity, high symmetry, and volatility of OsO_4 have led to extensive experimental investigations via photoelectron spectroscopy (PES),[1-7] and numerous calculational approaches have also been employed.[7-11] We recently published a combined theoretical and experimental study of OsO_4,[7] in which ΔSCF and Green's function methods were allied to synchrotron radiation-based PES to produce a consistent interpretation of the valence PE spectrum. The one aspect of our revised assignment that we were not confident about was the need to invoke substantial spin-orbit coupling in the lower ionization energy (IE) $^2T_2$ primary ion state and, consequently, a significant Os 6p atomic orbital (AO) contribution to the $3t_2$ molecular orbital (MO). We now have a fully relativistic implementation of the discrete variational (DV) Xα method of Ellis[12] at our disposal and have performed calculations to test our previous assertion.

Full details of the computational method have been given elsewhere.[13,14] The metal-ligand distance in OsO_4 is 1.711 Å.[15]

The valence electronic structure of formally d^0 MO_4 species is of the form

$$(1a_1)^2(1t_2)^6(1e)^4(2t_2)^6(2a_1)^2(3t_2)^6(1t_1)^6$$

where the numbering scheme ignores orbitals correlating with the core orbitals of the constituent atoms. $1a_1$ and $1t_2$ are essentially O 2s orbitals. Of the remaining occupied levels, the $2t_2$ and $2a_1$ are traditionally associated with M-O σ bonding, and the 1e and $3t_2$ with M-O π bonding, although there is no σ/π separability of the t_2 orbitals in T_d symmetry. In the absence of any f-orbital contribution from the central atom, the $1t_1$ MO is nonbonding. Five primary ion states are expected to occur in the valence region, viz. ^2E, $^2A_1$, $^2T_1$, and two $^2T_2$, corresponding to ionization of the 1e-$1t_1$ MOs.

The He I PE spectrum of OsO_4 is shown in Figure 1. There have been a number of differing assignments over the years.[1-7] Our most recent assignment places the 1e and $2t_2$ MOs under band E, a choice which immediately requires that the four bands A-D derive from the three remaining primary ion states, $^2T_1$ ($1t_1$), $^2T_2$ ($3t_2$), and $^2A_1$ ($2a_1$). We decided that band A arises from the $1t_1$ MOs and band D from the $2a_1$, leaving bands B and C assigned to the spin-orbit-split U′ and E″ components of the $^2T_2$ ($3t_2$) primary ion state.

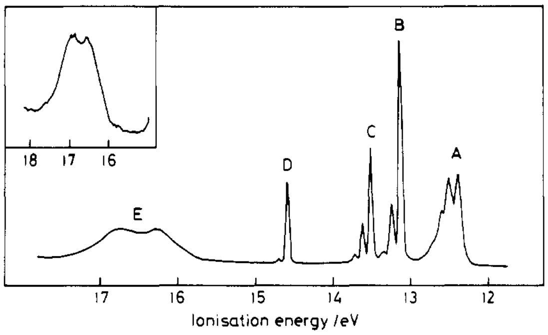

Figure 1. He I photoelectron spectrum of OsO_4. Reprinted with permission from ref 4. Copyright 1974 Royal Society of Chemistry.

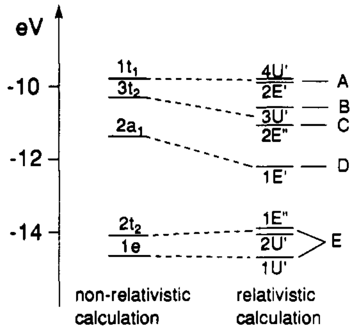

Figure 2. Eigenvalues of the valence molecular orbitals of OsO_4 from both nonrelativistic and relativistic discrete variational Xα calculations. Letters on the right-hand side refer to the associated bands in the photoelectron spectrum.

There are two principal problems with attributing the splitting of bands B and C to spin-orbit coupling. First, the magnitude of the separation (0.40 eV) is very large for what are found experimentally and predicted theoretically to be mainly O-localized orbitals. Second, it requires metal p character in the $3t_2$ MO to produce the observed ordering of the U′ and E″ levels.

We decided to investigate the effects of the inclusion of relativistic quantum mechanics on the electronic structure of OsO_4 via DV-Xα calculations. In particular, we sought support for our assertion of an Os 6p AO contribution to the $3t_2$ MO and whether it is sufficient to produce a 0.40-eV spin-orbit splitting.

The results of a nonrelativistic calculation are given in Table 1 and shown in Figure 2. They are consistent with those of many of the previous calculations, including our SCF and Green's function results. At the most negative eigenvalues come the Os-O bonding 1e and $2t_2$ MOs, both of which contain substantial Os 5d character. In particular, the Os-O π-bonding 1e orbital is found to be over 60% Os 5d. There is then a gap to the $2a_1$ level, which has no Os content. A small (ca. 7%) Os contribution is calculated in the $3t_2$ MO, and it is significant that the majority of this is predicted to be 6p rather than 5d. The remaining occupied level is the $1t_1$ MO, which is O-localized by symmetry.

Included in Table 1 are the calculated IEs of OsO_4, obtained using the transition-state method.[16] Quantitative agreement between the nonrelativistic theory and experiment is not perfect, although the predicted ion state ordering matches our spectral assignment.

[†] The Ohio State University.
[‡] University of Oxford.
(1) Diemann, E.; Müller, A. *Chem. Phys. Lett.* **1973,** *19,* 538.
(2) Foster, S.; Phelps, S.; Cusachs, L. C.; McGlynn, S. P. *J. Am. Chem. Soc.* **1973,** *95,* 5521.
(3) Evans, S.; Hammett, A.; Orchard, A. F. *J. Am. Chem. Soc.* **1974,** *96,* 6621.
(4) Burroughs, P.; Evans, S.; Hammett, A.; Orchard, A. F.; Richardson, N. V. *J. Chem. Soc., Faraday Trans. 2* **1974,** *70,* 1895.
(5) Egdell, R. G. D.Phil. Thesis, Oxford University, 1977.
(6) Green, J. C.; Kaltsoyannis, N.; MacDonald, M. A.; Sze, K. H. *Chem. Phys. Lett.* **1990,** *175,* 359.
(7) Green, J. C.; Guest, M. F.; Hillier, I. H.; Jarrett-Sprague, S. A.; Kaltsoyannis, N.; MacDonald, M. A.; Sze, K. H. *Inorg. Chem.* **1992,** *31,* 1588.
(8) Rauk, A.; Ziegler, T.; Ellis, D. E. *Theor. Chim. Acta* **1974,** *34,* 49.
(9) Weber, J. *Chem. Phys. Lett.* **1977,** *45,* 261.
(10) Arratia-Pérez, R. *Chem. Phys. Lett.* **1993,** *204,* 409.
(11) Pyykkö, P.; Li, J.; Bastug, T.; Fricke, B.; Kolb, D. *Inorg. Chem.* **1993,** *32,* 1525.
(12) Ellis, D. E. *J. Phys. B: At. Mol. Phys.* **1977,** *10,* 1.
(13) Schneider, W. F. Ph.D. Thesis, The Ohio State University, 1991.
(14) Schneider, W. F.; Strittmatter, R. J.; Bursten, B. E.; Ellis, D. E. *Density Functional Methods in Chemistry*; Springer-Verlag: New York, 1991; Chapter 16.
(15) Krebs, B.; Hasse, K. D. *Acta Crystallogr.* **1976,** *B32,* 1334.
(16) Slater, J. C. *Adv. Quantum Chem.* **1972,** *6,* 1. Slater, J. S. *The calculation of molecular orbitals*; Wiley: New York, 1979.

0020-1669/94/1333-2315$04.50/0

Table 1. Molecular Orbital Energies and Percent Compositions (Mulliken Population Analysis) of the Valence Levels of OsO_4

MO	energy (eV)	% Os	% O	Os contributions	IE (eV)[a]	IE_{expt} (eV)
			Calculated via the Nonrelativistic DV–Xα Approach			
$4t_2$	−4.082	46.41	53.59	42.06% 5d, 4.12% 6p		
2e	−6.277	38.67	61.33	38.67% 5d		
$1t_1$ (HOMO)	−9.783	0.00	100.00		−13.315	12.35
$3t_2$	−10.356	7.02	92.98	5.68% 6p, 0.92% 5d, 0.42% 5p	−13.684	13.11
						13.54
$2a_1$	−11.404	0.26	99.74		−14.986	14.66
$2t_2$	−14.158	45.13	54.87	41.57% 5d, 3.54% 6p, 0.02% 5p	−17.823	16.4–16.8
1e	−14.688	64.37	35.63	64.37% 5d	−18.512	16.4–16.8
			Calculated via the Relativistic DV–Xα Approach			
6U′ ($4t_2$)	−4.078	48.78	51.22	25.85% 5d, 17.99% $5\bar{d}$, 4.77% 6p		
3E″ ($4t_2$)	−4.180	51.91	48.09	44.43% 5d, 7.48% $6\bar{p}$		
5U′ (2e)	−6.172	40.91	59.09	21.68% $5\bar{d}$, 18.53% 5d		
4U′ ($1t_1$ HOMO)	−9.829	0.12	99.88		−13.437	12.35
2E′ ($1t_1$)	−9.956	0.06	99.94		−13.550	
3U′ ($3t_2$)	−10.578	7.38	92.62	7.02% 6p, 0.35% 5p	−14.116	13.11
2E″ ($3t_2$)	−11.058	10.38	89.97	9.17% $6\bar{p}$, 0.14% $5\bar{p}$, 0.65% 5d, 0.42% 5d	−14.565	13.54
1E′ ($1a_1$)	−12.275	5.79	94.21	5.71% 6s	−15.857	14.66
1E″ ($2t_2$)	−13.915	41.87	58.13	38.02% 5d, 0.57% $5\bar{d}$, 3.28% $6\bar{p}$	−17.553	16.4–16.8
2U′ ($2t_2$)	−14.065	45.36	54.64	36.30% 5d, 6.19% $5\bar{d}$, 2.87% 6p	−17.752	
1U′ (1e)	−14.709	60.02	39.98	45.19% $5\bar{d}$, 14.15% 5d, 0.68% 6p	−18.502	16.4–16.8

[a] Calculated via the transition-state method. [b] Unbarred labels refer to the higher angular momentum *j*-based atomic orbital; barred, to the lower.

The results of our relativistic calculation are given in Table 1 and shown in Figure 2. There are some substantial differences between the two calculations, which have important consequences for the interpretation of the PE spectrum. Of particular significance are the separation of the 2E″ and 3U′ orbital and the stabilization of the 1E′ level with respect to its $2a_1$ nonrelativistic equivalent.

The 1U′, 2U′, and 1E″ orbitals are the relativistic counterparts of the 1e and $2t_2$ MOs and are found to be similar in eigenvalue and composition.

The 1E′ MO is significantly more stable than its $2a_1$ nonrelativistic counterpart, by some 0.871 eV. This may be explained by the small Os 6s character of the relativistic MO, which is not present in the $2a_1$ level. The relativistic stabilization of the Os 6s AO is almost certainly the cause of this effect and is entirely consistent with our explanation of the cross-section behavior of band D in the PE spectrum as being due to a metal 6s contribution to the ionizing MO.

The effects of the inclusion of relativity on the $1t_1$ MO are seen to be small; the eigenvalues of the 2E′ and 4U′ levels are very similar to that of the nonrelativistic orbital.

Perhaps the most significant aspect of the relativistic calculation is the separation of the 2E″ and 3U′ orbitals, which are the spin–orbit-coupled components of the $3t_2$ MO. Not only are they split in an order consistent with p-orbital-derived coupling, but their 0.48-eV separation provides strong support for our assertions regarding bands B and C in the PE spectrum. The population analysis indicates that there is a slightly greater Os 6p involvement in the 2E″ and 3U′ levels than in the $3t_2$ and also suggests that a less than 10% contribution is sufficient to produce the observed splitting. It is encouraging that the $6\bar{p}$ and 6p contents of the 2E″ and 3U′ levels are matched almost exactly in the SW–Xα calculation of Arratia-Pérez.[10]

Table 1 also contains the calculated IEs of OsO_4. The experimental ion state ordering and relative separation are reproduced extremely well by the transition-state calculations although, as with the nonrelativistic calculations, the quantitative match is not exact. However, a uniform shift of ca. 1 eV to lower IE brings the experimental and theoretical data into close agreement. The splitting of the 2E″ and 3U′ orbitals is reduced to 0.45 eV in the transition-state calculations, in good agreement with the 0.40 eV found experimentally.

Pyykkö et al.[11] noted that only a very small 5p contribution is required in the $3t_2$ MO to lead to appreciable splitting, as the atomic 5p spin–orbit splitting is some 12.8 eV.[17]

We have performed a series of calculations ranging from the removal of both 5p and 6p Os AOs from the valence set through the inclusion of just the 5p and just the 6p in the calculation discussed above, which has both the 5p and 6p levels included in the valence functions.

When the Os 6p AOs are not included in the valence set, the calculation results are very different from those discussed above. The essentially 2E′ and 4U′ MOs (the relativistic equivalents of the $1t_1$ levels) are no longer the highest occupied MOs—a reversal of the relative ordering of the (2E′ + 4U′) and (2E″ + 3U′) orbitals occurs. Furthermore, the splitting of the 2E′ and 3U′ MOs is found to be very small (ca. 0.05 eV). Hence, our calculations indicate that the Os 6p AOs must be included in the valence set to obtain even qualitative agreement with experiment.

Placing the Os 5p AOs into the frozen core but retaining the 6p in the valence set produces results very similar to those given in Table 2 and Figure 2. However the splitting of the 2E″ and 3U′ MOs is reduced to 0.32 eV from the 0.48 eV found when the 5p AOs are included. Simplistically, therefore, our results indicate that mixing of the Os 5p AOs into the $3t_2$ MOs accounts for approximately one-third of the spin–orbit coupling. A combination of both 5p and 6p needs to be invoked to reproduce the full splitting.

It is worth noting that the relative energies of the valence MOs of OsO_4 are determined primarily by the type of metal AO involved in the MO. At the most negative eigenvalues come the MOs with significant 5d character—the 1e and $2t_2$. Subsequently comes the $2a_1$ level, which has Os 6s content. Then comes the $3t_2$ MO, which has sufficient Os 5p and 6p characters to produce a significant spin–orbit splitting. At the least negative eigenvalues are found the MOs with no metal character, the $1t_1$.

In summary, the DV–Xα calculations are in complete agreement with our assignment of the PE spectrum of OsO_4. They provide strong evidence for an Os *n*p AO derived spin–orbit splitting of the $^2T_2$ ($3t_2$) primary ion state, where *n* is both 5 and 6. Os–O multiple bonding is found in the 1e and $2t_2$ MOs, and the stabilization of the Os 6s AO with the inclusion of relativity provides an elegant rationalization of the observed cross-section behavior of the $2a_1^{-1}$ ionization.

Acknowledgment. N.K. thanks the Graduate School of The Ohio State University and SERC/NATO for Postdoctoral Fellowships. B.E.B. gratefully acknowledges the support of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG02-86ER13529).

---

(17) Desclaux, J.-P. *At. Data Nucl. Data Tables* **1973**, *12*, 311.