Valence Photoelectron Spectrum of OsO_4: Evidence for 5p Semicore Effects?

Pekka Pyykkö* and Jian Li†

Department of Chemistry, University of Helsinki,
Et. Hesperiankatu 4, 00100 Helsinki, Finland

T. Bastug, B. Fricke, and D. Kolb

Theoretische Physik, Gesamthochschule Kassel,
Heinrich-Plett-Strasse 40,
3500 Kassel-Oberzwehren, Germany

Received October 8, 1992

The photoelectron spectrum (PES) of OsO_4 has received a great deal of attention; see Green et al.[1] It consists of five bands, assigned as $1t_1 > 3t_2 > 2a_1 > 2t_2 > 1e$, in agreement with the quasirelativistic pseudopotential (PP) calculation in ref 1.

The puzzling feature was the apparent 0.4 eV spin–orbit (SO) splitting of the penultimate, $3t_2$, MO, with an intensity ratio of 2:1 or $\Gamma_8 > \Gamma_7$ ($u' > e''$), corresponding to an Os p AO and opposite to the 1:2 ratio, $\Gamma_7 > \Gamma_8$, for an Os d AO, predicted for $2t_2$. The calculated pseudopotential valence 6p character of 4.6 percent in the $3t_2$ and the atomic 6p SO splitting of about 0.93 eV were too small to explain the observed 0.4 eV.

We here consider the possibility that the observed splitting would be due to hybridization with the 5p semicore AO. An analogous 6p semicore participation is known to cause the 2:1 SO splitting of the $4t_{1u}$ HOMO of UF_6.[2] The Os $5p_{3/2}$ and U $6p_{3/2}$ radii are 1.211 and 1.897 au[3] while the Os–O and U–F distances are 3.233 and 3.772 au, respectively.

In order to verify this hypothesis, we performed the HF-level Gaussian 90 calculation for OsO_4 with both the small[4] and the large valence-space[5] PP of Hay and Wadt. We also report fully relativistic Dirac–Slater discrete-variational method (DS-DVM) results.[6] It should be noted that the $3t_2$ and $2t_2$ SO splittings were already successfully reproduced by SO-perturbed quasirelativistic multiple-scattering (QR–MS + SO) calculations by Topol' et al.[7] Fully relativistic MS results are being reported by Arratia-Perez.[8]

The valence orbital energies are shown in Figure 1. The SO splittings are given in Table I, and the orbital characters, both a Mulliken population and the diagonal c_i^2, in Table II.

The present DS–DVM splitting agrees well with experiment and with the QR–MS + SO ones. The $3t_2$ 5p and 6p Mulliken populations are too small to give the observed SO splittings but the diagonal DVM c_i^2, multiplied with the atomic splitting,[3] would give $0.043 \times 12.8 = 0.55$ eV. The large-PP c_i^2 is comparable with the DVM one.

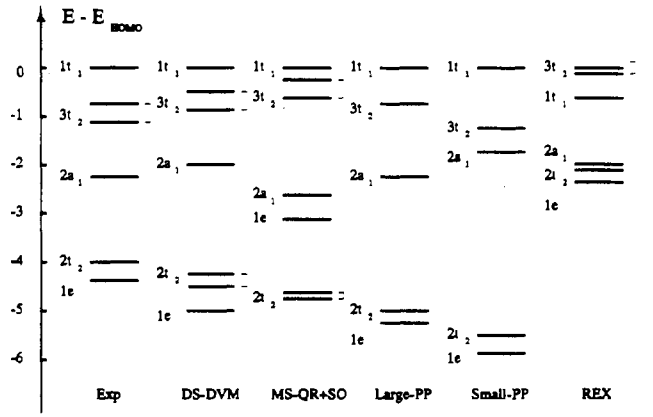

Figure 1. Experimental and calculated valence orbital energies (eV) of OsO_4.

Table I. SO Splittings (eV)

method	$2t_2$	$3t_2$
exptl[a]		0.40
DS–DVM	0.26	0.41
QR–MS + SO[b]	0.24	0.42
DS–MS[c]	0.34	0.32
REX	0.07	0.12

[a] Reference 1. [b] Reference 7. [c] Reference 8b.

Table II. SO-averaged Os character in valence t_2 MO's

MO	method	5p	6p	5d
$2t_2$	DS–DVM[a]	0.000	0.024	0.429
	QR–MS + SO[a,c]		0.006	0.367
	large PP[a]	0.000	0.013	0.419
$3t_2$	DS–DVM[a]	0.003	0.025	–0.003
	DS–DVM[b]	0.043	0.010	0.004
	QR–MS + SO[a,c]		0.077	0.000
	large-PP[a]	0.004	0.009	0.021
	large-PP[b]	0.053	0.002	0.033
	REX[a]	0.004	0.079	0.203
	REX[b]	0.018	0.049	0.396

[a] Mulliken population. [b] c_i^2. [c] Reference 7.

We also tested the small and large PP of ref 9. Here the 5p/6p separation appears to be less clear. The 5p c_i^2 in $3t_2$ becomes 0.085.

A third, or actually our first, way was to use the relativistic extended Hückel (REX) method.[10] With the parameters[11] it gives the MO order $3t_2 > 1t_1 > 2a_1 > 2t_2 > 1e$ (t_2 "pushing from below") with a 0.12 eV splitting of $3t_2$ in the correct order, $\Gamma_8 > \Gamma_7$. The diagonal 5p character in $3t_2$ is 0.017.

In these three methods (DVM, PP, REX), the $3t_2$ SO splitting is thus obtained by hybridization with the deep-lying, semicore 5p AO, as suspected. In the MS methods, the numerical valence "6p" component is variationally optimized and the same physics is obtained without explicit 5p character. Indeed, the MS valence p AOs can be much more contracted than the free-atom ones.[12]

† On leave of absence from: Department of Chemistry, Peking University, Beijing 100871, PRC.

(1) 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.
(2) For early references, see Case, D. A.; Yang, C. Y. *J. Chem. Phys.* **1980**, *72*, 3443.
(3) Desclaux, J. P. *At. Data Nucl. Data Tables* **1973**, *12*, 311.
(4) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. Same oxygen basis and Os basis modification as in ref 1.
(5) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. A triple-ζ (5411/411/211) basis for Os; same diffuse s, p, and d functions as in ref. 1.
(6) Rosén, A.; Ellis, D. E. *J. Chem. Phys.* **1975**, *62*, 3039.
(7) Topol', I. A.; Vovna, V. I.; Kazachek, M. V. *Teor. Eksp. Khim.* **1987**, *23*, 456; *Theor. Exp. Chem. (Engl. Transl.)* **1987**, *23*, 427.
(8) (a) Arratia-Perez, R. Presented at the XIX Congreso LatinoAmericano de Qúimica, Buenos Aires, 1990; Paper p1601. (b) Arratia-Perez, R. *Chem. Phys. Lett.* **1993**, *203*, 409.
(9) Ross, R. B.; Powers, J. M.; Atashroo, T.; Ermler, W. C.; LaJohn, L. A.; Christiansen, P. A. *J. Chem. Phys.* **1990**, *93*, 6654. In "small valence-space", a (211/211/211) basis for Os was used, with the same diffuse s, p, and d functions as in ref 1. In "large valence-space", a (5311/311/211) basis for Os was used.
(10) Pyykkö, P.; Lohr, L. L. *Inorg. Chem.* **1981**, *20*, 1950.
(11) Default Os parameters from ref 10 with added 5p (α = –71.707 and –58.885 eV, ζ = 4.935 and 4.543 for $5p_{1/2}$ and $5p_{3/2}$, respectively). Oxygen 2p: α = –11.784 and –11.745 eV; ζ = 1.5302(0.7262) + 3.5852(0.3511) and 1.6274(0.7256) + 3.5741(0.3516). No 2s was used. The "Δ-formula" for h_{ab} was used.
(12) Bowmaker, G. A.; Boyd, P. D. W.; Sorrenson, R. J. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1627.

0020-1669/93/1332-1525$04.00/0

The SO splitting of the $2t_2$ has $\Gamma_7 > \Gamma_8$ and can be directly related to the 5d character; e.g., $0.429 \times 1.05 = 0.45$ eV.

Concomitantly, a hole is introduced to the 5p AO. As this AO has an $\langle r^{-3} \rangle$ of 137.6 au^3, the Os nuclear quadrupole coupling may give in asymmetrical osmyl compounds further evidence, as suggested for the actinyl compounds.[13,14]

Acknowledgment. The calculations were performed on the Convex 3820 at the Centre for Scientific Computing, Espoo, Finland. J.L. is supported by Centre for International Mobility (CIMO), Helsinki, Finland. T.B. acknowledges funding from the DFG. We thank Ramiro Arratia-Perez for stimulating correspondence.

(13) Larsson, S.; Pyykkö, P. *Chem. Phys.* **1986**, *101*, 355.

(14) Pyykkö, P.; Jové, J. *New J. Chem.* **1991**, *15*, 717.