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# Comment on “Computational and spectroscopic tools for detection of bond covalency in Pu(IV) materials,” by P. S. Bagus, B. Schacherl and T. Vitova, Inorg. Chem. 2021, 60, 16090–16102.

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## **Abstract**

In their article of 2021, Bagus, Schacherl and Vitova present results for PuO<sub>2</sub> that indicate that the plutonium is in a Pu<sup>4+</sup> state with the number of 5f electrons (n) being n = 4 (5f<sup>4</sup>). This result is inconsistent with our recent results and, moreover, with the outcome that n = 5 (5f<sup>5</sup>) from earlier Branching Ratio measurements.

## **Introduction**

Besides being radioactive and chemically toxic, plutonium dioxide is complicated. In vacuo, i.e. under reducing conditions, it is well documented that Pu will form at least three co-existing metastable components, Pu metal, Pu sesquioxide (Pu<sub>2</sub>O<sub>3</sub>) and Pu dioxide (PuO<sub>2</sub>). [1,2] Under oxidizing conditions, e.g. at atmospheric pressure in the presence of water, plutonium dioxide has a propensity to become non-stoichiometric, PuO<sub>2+x</sub>, with x as large as 0.27. This non-stoichiometry is associated with the formation of the Pu(VI) oxidation state in addition to the usual Pu(IV) in PuO<sub>2</sub>. [3]

## **Discussion**

Our recent work on ThO<sub>2</sub>, UO<sub>2</sub> and PuO<sub>2</sub> indicates the powerful connection between High Energy Resolution Fluorescence Detection (HERFD) and Inverse Photoelectron Spectroscopy (IPES). [4] This connection is so strong that the theory for HERFD can accurately predict the leading-edge fine structure in IPES, an example of which is shown in Figure 1. The rise in the IPES as the energy increases to 4 eV and above is due to the Pu6d-O2p manifold, not the Pu5f-O2p as in the structure near zero eV. Under the ultra-high vacuum conditions of the IPES experiment, it was possible to isolate the contributions from Pu metal, Pu<sub>2</sub>O<sub>3</sub> and PuO<sub>2</sub>. Thus, the IPES spectrum in Figure one is reliably from PuO<sub>2</sub>, not some other component.

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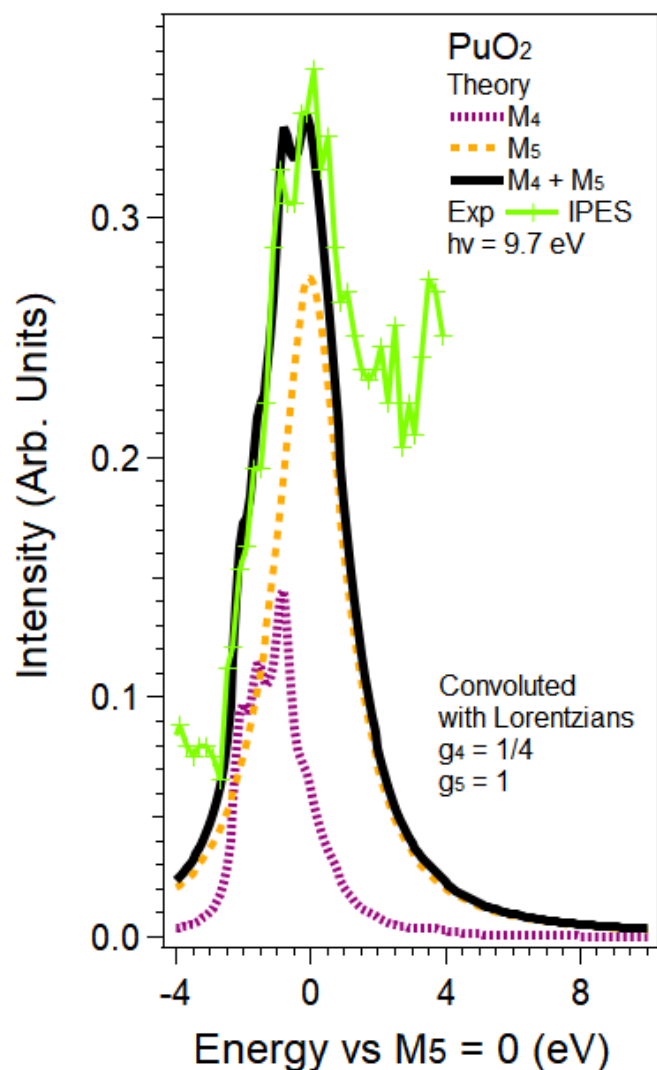


Figure 1

Shown here is a comparison of the experimental Inverse Photoelectron Spectroscopy (IPES) and theory curves for PuO<sub>2</sub>. The HERFD Theory curves include contributions from the PuM<sub>4</sub> and PuM<sub>5</sub> edges as well as their sum. Note the strong agreement in the leading edges at energies near to -2 eV.

Note the absence of strong structure on the following edges in the M<sub>4</sub> (E > -1 eV), the M<sub>5</sub> and the sum of M<sub>4</sub> and M<sub>5</sub> curves (E > 0 eV). This absence of a strong shoulder on the following edges is inconsistent with the results of Bagus, Schacherl and Vitova (BSV, their Figure 7). Using atomic calculations for Pu<sup>3+</sup> (n = 5) and Pu<sup>4+</sup> (n = 4), it is possible to understand the discrepancy between the theory curves of BSV and those in Figure 1. Both of the Pu<sup>4+</sup> curves in Figure 2 are in very good agreement with the theory curves of BSV, including the following shoulder in the M<sub>4</sub> spectrum. The following shoulder in the M<sub>4</sub> Pu<sup>4+</sup> theory originates from angular momentum coupling. Neither the Pu<sup>4+</sup> M<sub>5</sub> curve in Figure 2a nor the theory curves of BSV can explain the observation of the shoulder in the M<sub>5</sub> experimental curve of BSV.

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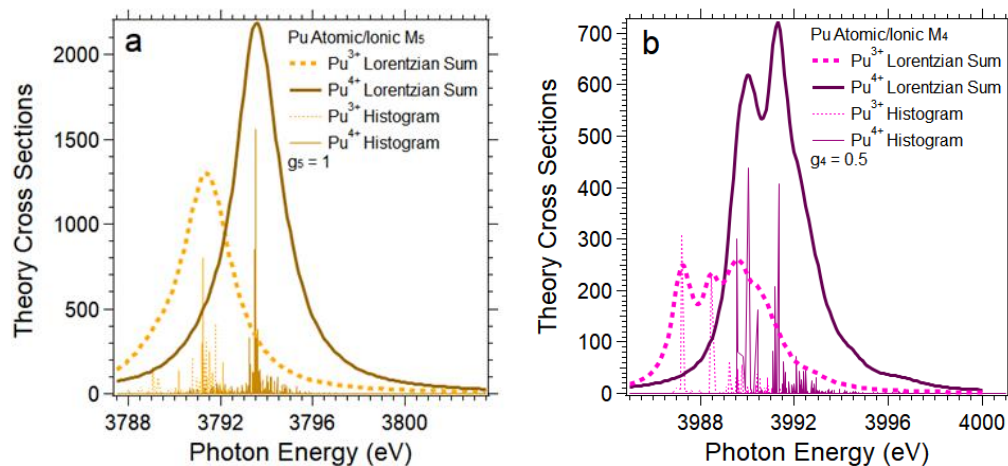


Figure 2 The results of atomic theory calculations are presented here, for Pu<sup>3+</sup> and Pu<sup>4+</sup>. See text and legends for details. The Lorentzian  $g_i$ 's are the half-width-at-half-heights for the  $i$  transition.

At this point, it is clear that the theory of BSV has been driven to a Pu<sup>4+</sup>  $n = 4$  state and our result is close to the Pu<sup>3+</sup>  $n = 5$  state. Which brings the discussion back to the earlier Branching Ratio measurements, shown in Figure 3 along with the results of a modified FEFF simulation. [5]

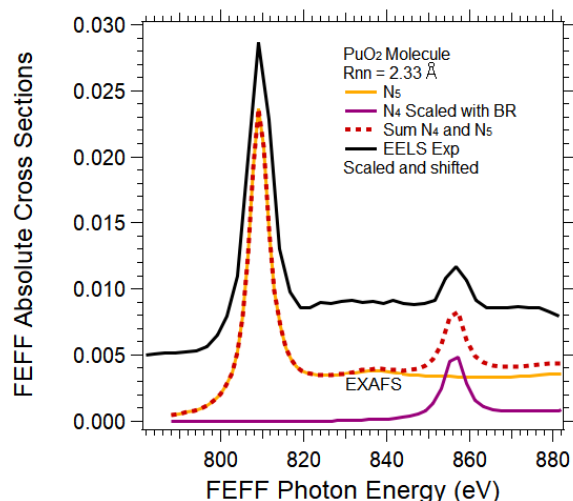


Figure 3

Here is a comparison of the Electron Energy Loss measurements of solid PuO<sub>2</sub> [6] and a modelling performed using FEFF simulations for a PuO<sub>2</sub> molecule with a nearest neighbor distance of  $R_{nn} = 2.33 \text{ \AA}$ . The N<sub>4</sub> result has been scaled to be consistent with the correct Branching ratio of BR = 0.82.

The Electron Energy Loss (EELS) measurements were done in a Transmission Electron Microscope with a primary beam energy of 100,000 eV. [6] This energy level assures both bulk sensitivity and the convergence to the electric dipole limit for EELS, thus rendering it equivalent to X-Ray Absorption Spectroscopy. [7] Regarding this work [6], there have been some questions concerning its data analysis procedures [8,9], so to circumvent that issue the data was reanalyzed following the guidance provided by the FEFF simulation in Figure 3. The result of that process was the determination that  $BR = 0.85 \pm 0.05$ , consistent with  $n = 5$  ( $BR = 0.81$ ) but not  $n = 4$  ( $BR = 0.76$ ), from the Intermediate Coupling Model. [9 - 11]. Thus, the Pu<sup>4+</sup> theory of BSV is not appropriate.

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The only remaining question is the source of the two following shoulders in the  $M_4$  and  $M_5$  spectra of BSV. In all likelihood, it is a higher oxidation state contaminant, probably Pu(VI). Haschke, Allen and Morales [3] have discussed the non-stoichiometric behavior of  $\text{PuO}_{2+x}$ , and suggest that the  $x$  comes from Pu(VI) generated by surface corruption at atmospheric pressure and in the presence of water. It is known that HERFD has an enhanced surface sensitivity relative to the higher energy hard x-ray measurements [5] and Kvashnina and coworkers [12] have shown that higher oxidation state features can be seen at slightly higher photon energies in HERFD.

## Acknowledgements

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## References

1. H. G. García Flores, P. Roussel, D. Moore, and D. L. Pugmire, *Surf. Sci.* 605, 314 (2011).
2. P. Roussel, *J. Electron Spectroscopy Rel. Phen.* 246, 147030 (2021).
3. J.M. Haschke, T.A. Allen, and L. A. Morales, *Science* 287, 285 (2000)
4. J. G. Tobin, H. Ramanantoanina, C. Daul, S.-W. Yu, P. Roussel, S. Nowak, R. Alonso-Mori, T. Kroll, D. Nordlund, T.-C. Weng, D. Sokaras, *Phys. Rev. B* 105, 125129 (2022).
5. J. G. Tobin, S. Nowak, S.-W. Yu, R. Alonso-Mori, T. Kroll, D. Nordlung, T.-C. Weng, D. Sokaras, *Surface Science* 698, 121607 (2020).
6. K. T. Moore, G. van der Laan, R. G. Haire, M. A. Wall, and A. J. Schwartz, *Phys. Rev. B* 73, 033109 (2006).
7. K.T. Moore, B.W. Chung, S.A. Morton, S. Lazar, F.D. Tichelaar, H.W. Zandbergen, P. Söderlind, G. van der Laan, A.J. Schwartz, and J.G. Tobin, *Phys. Rev. B* 69, 193104 (2004).
8. J.G. Tobin, *J. Electron Spectroscopy and Rel. Phen.*, 194, 14 (2014).
9. J.G. Tobin, S.-W. Yu, C.H. Booth, T. Tyliczszak, D.K. Shuh, G. van der Laan, D. Sokaras, D. Nordlund, T.-C. Weng, and P. S. Bagus, *Phys. Rev. B* 92, 035111 (2015).
10. G. van der Laan, K.T. Moore, J.G. Tobin, B.W. Chung, M.A. Wall, and A.J. Schwartz, *Phys. Rev. Lett.* 93, 097401 (2004).
11. J.G. Tobin, K.T. Moore, B.W. Chung, M.A. Wall, A.J. Schwartz, G. van der Laan, and A.L. Kutepov, *Phys. Rev. B* 72, 085109 (2005).
12. K.O. Kvashnina, S.M. Butorin, P. Martin, P. Glatzel, *Phys. Rev. Lett.* 111, 253002 (2013).