Ab initio studies on new actinide species

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Fully relativistic, four-component Dirac-Fock calculations and quasirelativistic pseudopotential calculations at different ab initio levels are used to study the bonding trends among the naked, triatomic $[OAnO]^{q+}$ groups, or the oxyfluorides $[AnO_nF_m]^q$ with f^0 configurations. The triatomic f^0 series is suggested to range from the bent ThO_2 via the linear $OPaO^+$ to at least NpO_2^{3+}, a possible new gas-phase species. The neutral oxyfluoride molecules include the experimentally unknown NpO_2F_3 and PuO_2F_4. The latter is a candidate for the so far unknown oxidation state Pu(VIII), which is found to lie considerably above Pu(VI), but to be locally stable. Their all-oxygen isoelectronic analogues are the known NpO_5^{3-} and the unknown PuO_6^{4-} . Other possible candidates for Pu(VIII) are PuO_4 (D_{4h}) and PuF_8(O_h)