Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information: Evidence of Vacancy Ordered Structures in PuO_{2-x} and AmO_{2-x} from First-principles Calculations

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TABLE S1. The structural details (Lattice type, Space group, and Lattice parameters) of the three predicted ground states of PuO_{2-x}.

Predicted GS	Lattice Parameters	Atomic Positions
PuO_2	a=b=3.847,c=5.515 Å	Pu (2a) 0 0 0
I4/mmm (139)	α=β=γ=90.0	O (4a) 0 1/2 1/4
Pu_8O_{15}	a=7.757,b=11.028,	Pu (4c) 0.37851 0.37813 0.75677, Pu (4c) 0.73551 0.11419 0.00004
C2 (5)	c=8.670 Å,	Pu (4c) 0.13654 0.38036 0.27326, Pu (2b) 0.00000 0.62824 0.50000
	β=116.30	Pu (2b) 0.00000 0.12836 0.50000
	V_0=667.15	O (2a) 0.00000 0.00534 0.00000, O (2a) 0.00000 0.75661 0.00000
		O (2a) 0.00000 0.46794 0.00000, (4c) 0.64797 0.25223 0.75571
		O (4c) 0.11521 0.49773 0.73638, (4c) 0.74113 0.25357 0.48134
		O (4c) 0.75384 0.00574 0.50826, (4c) 0.10730 0.25223 0.75476
		O (4c) 0.62139 0.49760 0.73718
Pu_6O_{11}	a=12.240,b=5.531,	Pu (4c) 0.66594 0.32681 0.58421, Pu (4c) -0.00172 0.31584 0.73545
C2 (5)	c=7.853 Å,	Pu (4c) 0.32190 0.35606 -0.08926,
	β=108.6	O (4c) 0.64867 0.08574 0.83784, O (4c) 0.34775 0.07446 0.68654
		O (2b) 0.00000 0.57120 0.50000, O (4c) 0.82477 0.08173 0.64809
		O (2b) 0.00000 0.06526 0.50000, O (4c) 0.83727 0.08406 0.18325
		O (2a) 0.00000 0.13084 0.00000
Pu_8O_{14}	a=b=7.804,	Pu (4k) 0.76482 0.50000 0.72208, Pu (4j) 0.73833 0.00000 0.77773
P-4m2 (115)	c=5.592 Å,	O (2g) 0.00000 0.50000 0.45827, O (4i) 0.78938 0.78938 0.50000
	V_0=340.58	O (1c) 0.50000 0.50000 0.50000, O (4h) 0.73802 0.73802 0.00000
		O (2g) 0.00000 0.50000 -0.01481, O (1a) 0.00000 0.00000 0.00000
Pu_2O_3	a=b=3.935,c=5.723 Å	Pu (2g) 0 1/2 0.27719
P-4m2 (115)	α=β=γ=90.0	O (1d) 0 0 1/2, O (1b) 1/2 1/2 0
		O (1c) 1/2 1/2 1/2

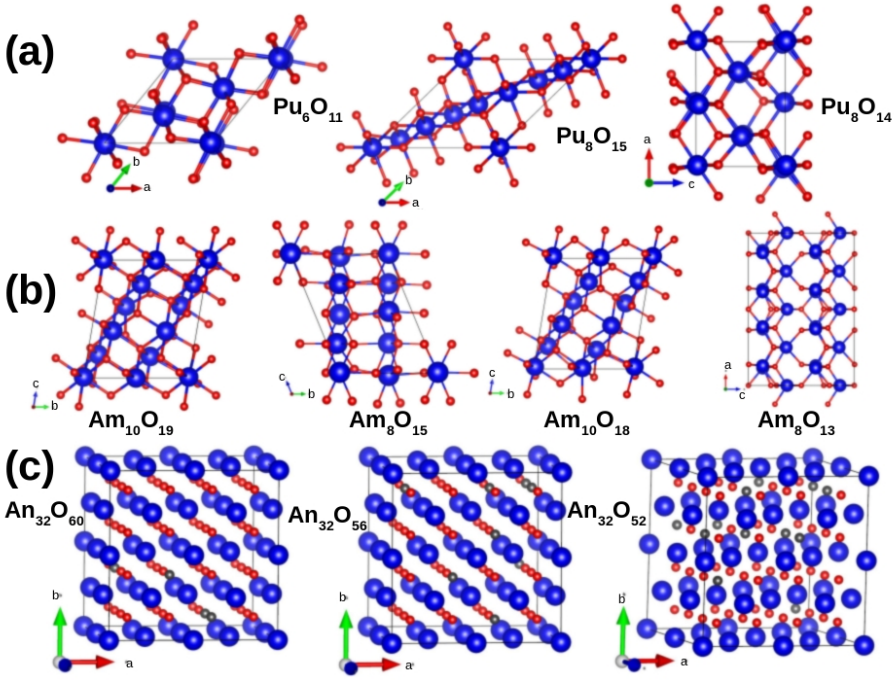

FIG. S1. The CE determined vacancy ordered structures of (a) PuO_{2-x} (b) AmO_{2-x} and (c) SQS generated structures are shown here. Oxygen and An (Pu/Am) atoms are shown in red and blue, respectively.

Elastic constant matrices for AnO_{2-x} in GPa $=$

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix}$$

$PuO_2=$

$$\begin{bmatrix} 372.965 & 110.649 & 109.661 & -0.362 & 0.078 & 0.507 \\ 110.649 & 372.332 & 109.350 & 0.043 & 0.087 & 0.032 \\ 109.661 & 109.350 & 378.729 & 0.099 & 0.141 & 0.513 \\ -0.362 & 0.043 & 0.099 & 69.770 & 0.079 & 0.512 \\ 0.078 & 0.087 & 0.141 & 0.079 & 69.535 & 0.099 \\ 0.507 & 0.032 & 0.513 & 0.512 & 0.099 & 68.382 \end{bmatrix}$$

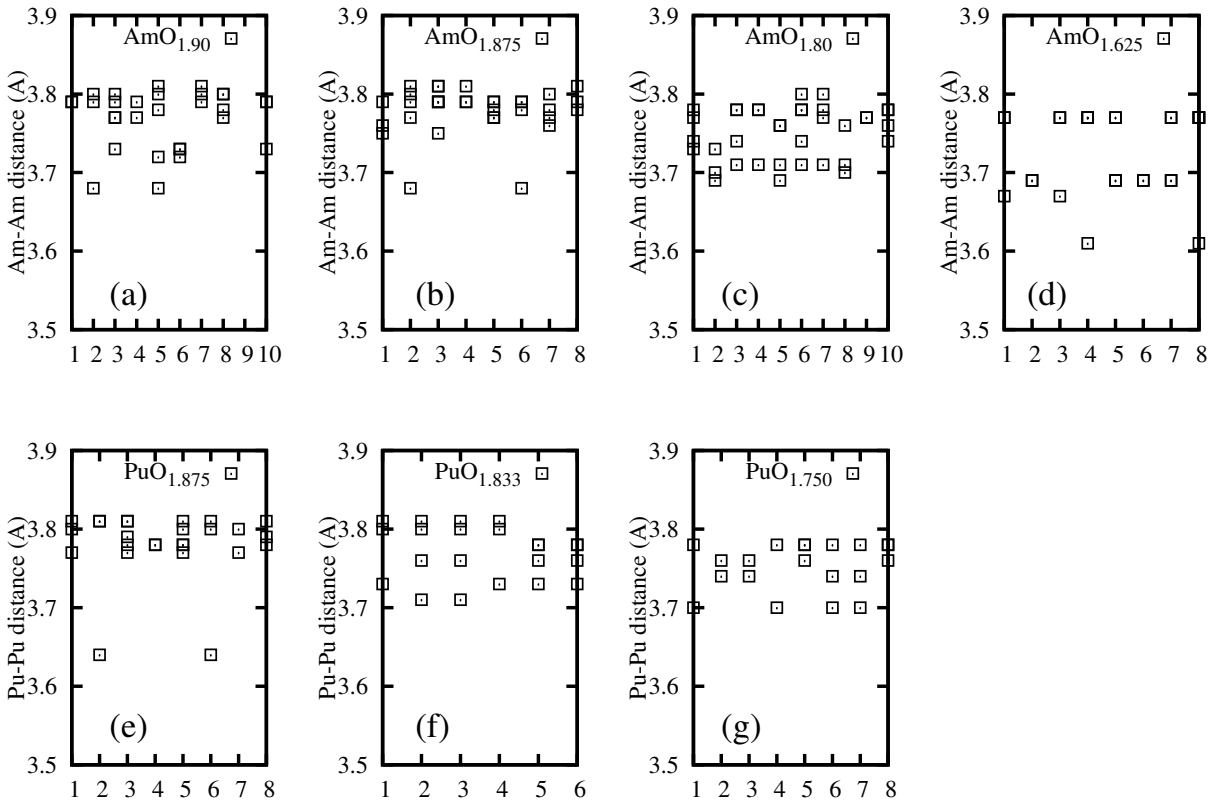

FIG. S2. Distribution of Ac-Ac distances in vacancy ordered structures (a) $Am_{10}O_{19}$ ($AmO_{1.90}$), (b) Am_8O_{15} ($AmO_{1.875}$), (c) $Am_{10}O_{18}$ ($AmO_{1.8}$), (d) Am_8O_{13} ($AmO_{1.625}$) and (e) Pu_8O_{15} ($PuO_{1.875}$), (f) Pu_6O_{11} ($PuO_{1.833}$), (g) Pu_8O_{14} ($PuO_{1.75}$) in AmO_{2-x} and PuO_{2-x}, respectively. The x-axis shows the Number of Am/Pu atoms present in the vacancy ordered structures.

$$\mathrm{Pu_8O_{15}}= \begin{bmatrix} 274.947 & 144.159 & 111.112 & -1.123 & 0.208 & 0.285 \\ 144.159 & 257.147 & 103.015 & 1.306 & -0.254 & -0.793 \\ 111.112 & 103.015 & 301.561 & 2.307 & 0.132 & -0.128 \\ -1.123 & 1.306 & 2.307 & 56.689 & 0.377 & 0.013 \\ 0.208 & -0.254 & 0.132 & 0.377 & 64.482 & 0.386 \\ 0.285 & -0.793 & -0.128 & 0.013 & 0.386 & 88.005 \end{bmatrix}$$

$$\mathrm{Pu_6O_{11}}= \begin{bmatrix} 248.293 & 132.486 & 103.564 & -0.876 & 3.406 & 4.288 \\ 132.486 & 248.492 & 103.575 & -3.360 & 0.886 & 4.348 \\ 103.564 & 103.575 & 274.994 & -1.944 & 2.011 & -2.467 \\ -0.876 & -3.360 & -1.944 & 58.009 & 3.044 & -0.081 \\ 3.406 & 0.886 & 2.011 & 3.044 & 57.934 & 0.073 \\ 4.288 & 4.348 & -2.467 & -0.081 & 0.073 & 91.540 \end{bmatrix}$$

$$\mathrm{Pu_8O_{14}\ (P\text{-}4m2)}= \begin{bmatrix} 224.290 & 111.405 & 101.879 & 0.000 & 0.000 & -0.097 \\ 111.405 & 224.290 & 101.879 & 0.000 & 0.000 & -0.096 \\ 101.879 & 101.879 & 258.176 & 0.000 & 0.000 & -0.085 \\ 0.000 & 0.000 & 0.000 & 55.723 & 0.150 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.150 & 55.739 & 0.000 \\ -0.097 & -0.096 & -0.085 & 0.000 & 0.000 & 66.343 \end{bmatrix}$$

$$\mathrm{Pu_2O_3}= \begin{bmatrix} 170.270 & 98.521 & 98.216 & -0.211 & 0.022 & 0.118 \\ 98.521 & 168.513 & 98.048 & 0.239 & 0.132 & -0.141 \\ 98.216 & 98.048 & 169.275 & -0.054 & -0.080 & 0.056 \\ -0.211 & 0.239 & -0.054 & 47.831 & -0.636 & 0.664 \\ 0.022 & 0.132 & -0.080 & -0.636 & 48.121 & -0.516 \\ 0.118 & -0.141 & 0.056 & 0.664 & -0.516 & 48.037 \end{bmatrix}$$

$$\mathrm{Am_{10}O_{19}}= \begin{bmatrix} 258.826 & 149.574 & 107.321 & -0.128 & 2.325 & -0.025 \\ 149.574 & 257.532 & 106.521 & -0.441 & -1.753 & -2.003 \\ 107.321 & 106.521 & 297.723 & -0.598 & -0.692 & 2.792 \\ -0.128 & -0.441 & -0.598 & 52.287 & 1.108 & -0.807 \\ 2.325 & -1.753 & -0.692 & 1.108 & 58.733 & 2.055 \\ -0.025 & -2.003 & 2.792 & -0.807 & 2.055 & 97.090 \end{bmatrix}$$

$$\mathrm{Am_8O_{15}}= \begin{bmatrix} 264.370 & 144.133 & 105.103 & 2.519 & -3.344 & -0.190 \\ 144.133 & 241.498 & 105.925 & -1.156 & -1.932 & -2.931 \\ 105.103 & 105.925 & 292.172 & -0.790 & 0.767 & 2.440 \\ 2.519 & -1.156 & -0.790 & 59.482 & 0.122 & -0.005 \\ -3.344 & -1.932 & 0.767 & 0.122 & 60.606 & 0.709 \\ -0.190 & -2.931 & 2.440 & -0.005 & 0.709 & 87.048 \end{bmatrix}$$

$$\mathrm{Am_{10}O_{18}}= \begin{bmatrix} 229.415 & 116.782 & 91.602 & -3.932 & -8.159 & -0.806 \\ 116.782 & 197.330 & 78.551 & -0.580 & -2.781 & -1.968 \\ 91.602 & 78.551 & 239.688 & -2.374 & -4.362 & 3.744 \\ -3.932 & -0.580 & -2.374 & 46.542 & -5.088 & -0.455 \\ -8.159 & -2.781 & -4.362 & -5.088 & 56.171 & 0.985 \\ -0.806 & -1.968 & 3.744 & -0.455 & 0.985 & 78.348 \end{bmatrix}$$

$$\mathrm{Am_{8}O_{13}}= \begin{bmatrix} 184.236 & 94.951 & 74.587 & 0.031 & -0.139 & -0.063 \\ 94.951 & 186.346 & 74.904 & -0.070 & -0.097 & -0.089 \\ 74.587 & 74.904 & 198.344 & -0.031 & -0.073 & -0.098 \\ 0.031 & -0.070 & -0.031 & 38.055 & 0.041 & -0.024 \\ -0.139 & -0.097 & -0.073 & 0.041 & 38.641 & -0.112 \\ -0.063 & -0.089 & -0.098 & -0.024 & -0.112 & 63.964 \end{bmatrix}$$

Elastic constant matrices for $\mathrm{Am_2O_3}$ (Sp. Gr. P-3m1) in GPa $= \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & C_{66} \end{bmatrix}$

$$\mathrm{Am_2O_3}= \begin{bmatrix} 225.266 & 126.198 & 87.798 & 35.660 & 0.000 & 0.000 \\ 126.198 & 225.266 & 87.798 & -35.660 & 0.000 & 0.000 \\ 87.798 & 87.798 & 141.140 & 0.000 & 0.000 & 0.000 \\ 35.660 & -35.660 & 0.000 & 66.908 & 0.000 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.000 & 66.910 & 35.660 \\ 0.000 & 0.000 & 0.000 & 0.000 & 35.660 & 49.534 \end{bmatrix}$$

$$\mathrm{AmO_2}= \begin{bmatrix} 355.760 & 107.274 & 102.814 & 0.000 & 0.000 & 0.108 \\ 107.274 & 354.489 & 113.638 & 0.000 & 0.000 & -0.049 \\ 102.814 & 113.638 & 315.913 & 0.001 & 0.000 & -0.496 \\ 0.000 & 0.000 & 0.001 & 44.473 & 0.272 & 0.000 \\ 0.000 & 0.000 & 0.000 & 0.272 & 56.156 & 0.000 \\ 0.108 & -0.049 & -0.496 & 0.000 & 0.000 & 61.704 \end{bmatrix}$$

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TABLE S2. The structural details (Lattice type, Space group, and Lattice parameters) of the three predicted ground states of AmO_{2-x}.

Predicted GS	Lattice Parameters	Atomic Positions
AmO_2	a=b=3.883,c=5.593 Å	Am (2a) 0 0 0
I4/mmm (139)	α=β=γ=90.0	O (4a) 0 1/2 1/4
$Am_{10}O_{19}$	a=6.6665,b=7.7658,	Am(1a) 0.60715 0.39800 0.79539, Am(1a) 0.19947 0.28390 0.60840
P1 (1)	c=8.6812,	Am(1a) 0.41378 0.59954 0.18192, Am(1a) 0.00400 0.49823 -0.00120
	α=76.83,	Am(1a) 0.20009 0.80912 0.61272, Am(1a) 0.76912 0.70712 0.39669
	β=75.36,	Am(1a) 0.00002 -0.00224 0.00728, Am(1a) 0.61028 0.89813 0.79966
	γ=72.92,	Am(1a) 0.80084 0.20186 0.40002, Am(1a) 0.39324 0.10244 0.19826
	V_0=409.9057 $Å_3$	O(1a) 0.86831 0.40908 0.54729, O(1a) 0.25120 0.50198 0.71742
		O(1a) -0.05226 0.28716 0.85082, O(1a) -0.04067 0.80837 0.85432
		O(1a) 0.65025 0.60456 -0.06225, O(1a) 0.06381 0.70352 0.16755
		O(1a) 0.74388 0.49234 0.24587, O(1a) 0.72425 0.01723 0.25384
		O(1a) 0.40465 0.78734 0.35690, O(1a) 0.87485 0.88132 0.54712
		O(1a) 0.53953 0.70516 0.65578, O(1a) 0.57182 0.19152 0.64525
		O(1a) 0.25821 0.00148 0.75594, O(1a) 0.64860 0.09734 -0.04954
		O(1a) 0.36090 -0.09729 0.04590, O(1a) 0.36733 0.39408 0.04245
		O(1a) 0.05107 0.18683 0.15889, O(1a) 0.41706 0.32914 0.36148
		O(1a) 0.14923 0.10274 0.45584
Am_8O_{15}	a=6.72692,b=6.73147,	Am(1a) 0.24272 0.25118 0.49351, Am(1a) 0.14913 0.62881 0.25099
P1 (1)	c=8.63044,	Am(1a) 0.48766 0.49463 -0.02054, Am(1a) 0.37208 0.87797 0.75038
	α=105.16247,	Am(1a) 0.75307 0.76455 0.51749, Am(1a) 0.62033 0.10059 0.24783
	β=104.98819,	Am(1a) -0.00195 0.00791 0.00589, Am(1a) 0.87472 0.37740 0.75114
	γ=109.29372,	O(1a) -0.02604 0.26639 0.24144, O(1a) 0.07452 0.82360 0.46797
	V_0=329 $Å_3$	O(1a) 0.38464 0.63474 0.49665, O(1a) -0.00460 0.76097 0.77378
		O(1a) 0.23232 0.49559 0.74751, O(1a) 0.41678 0.17051 0.03144
		O(1a) 0.62712 0.86723 0.00108, O(1a) 0.25510 -0.01241 0.24188
		O(1a) 0.52134 0.72438 0.24629, O(1a) 0.65457 0.39207 0.47673
		O(1a) 0.85897 0.11543 0.50204, O(1a) 0.50321 0.26072 0.73907
		O(1a) 0.76179 0.01460 0.76348, O(1a) 0.86489 0.60919 0.02534
		O(1a) 0.12764 0.37395 -0.00139

TABLE S3. The structural details (Lattice type, Space group, and Lattice parameters) of the three predicted ground states of AmO_{2-x}.

Predicted GS	Lattice Parameters	Atomic Positions
$Am_{10}O_{18}$	a=6.780,b=7.769,	Am(1a) 0.61930 0.40711 0.78888, Am(1a) 0.19605 0.28506 0.61416
P1 (1)	c=8.709 Å	Am(1a) 0.42221 0.59905 0.17313, Am(1a) 0.00999 0.48691 0.00834
	α=76.92,	Am(1a) 0.20686 0.81249 0.59399, Am(1a) 0.77254 0.70720 0.39219
	β=74.72,	Am(1a) 0.00321 0.00795 0.01983, Am(1a) 0.58372 -0.09411 0.79595
	γ=73.26,	Am(1a) 0.79712 0.20691 0.40534, Am(1a) 0.39654 0.10455 0.20661
	V_0=418.18 $Å_3$	O(1a) 0.85727 0.40866 0.55036, O(1a) 0.21008 0.53784 0.72709
		O(1a) -0.06594 0.29049 0.86955, O(1a) 0.67540 0.61994 -0.07524
		O(1a) 0.05365 0.71179 0.14385, O(1a) 0.74968 0.48713 0.25351
		O(1a) 0.73000 0.02243 0.26076, O(1a) 0.42214 0.79365 0.35071
		O(1a) 0.86594 0.88110 0.56820, O(1a) 0.53603 0.70435 0.64959
		O(1a) 0.55357 0.20314 0.65698, O(1a) 0.22324 -0.02139 0.76825
		O(1a) 0.71708 0.02756 -0.06324, O(1a) 0.35466 -0.07402 0.04268
		O(1a) 0.38978 0.37629 0.02243, O(1a) 0.05634 0.19586 0.16953
		O(1a) 0.41691 0.31773 0.35198, O(1a) 0.14663 0.09433 0.45457
Am_8O_{13}	a=16.056,b=7.734,	Am (8d) 0.38567 0.0 0.13730, Am (8b) 0.25 0.25 0.35875
Fmm2 (42)	c=11.164 Å,	Am (8c) 0.0 0.26653 0.86702, Am (8d) 0.87036 0.00 0.13703
	α=β=γ=90	O (8d) 0.25272 0.0 0.24060, O (16e) 0.86239 0.21986 0.00528
	V_0=1386 $Å_3$	O (16e) 0.37693 0.26314 0.25311, O (4a) 0.0 0.0 0.76819
		O (4a) 0 0 0.50238, O (4a) 0 0 0.21445
Am_2O_3	a=b=3.919,c=5.718 Å	Am (2g) 0 1/2 0.279
P-4m2 (115)	α=β=γ=90.0	O (1d) 0 0 1/2, O (1b) 1/2 1/2 0
		O (1c) 1/2 1/2 1/2