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

Supporting Information for:

Correlation Effects in the Photoelectron Spectrum and Photoionization Dynamics of OsO_4

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Table S1: Binding energy calculated in previous studies and their comparison with the experimental energy of the photoelectron bands of OsO_4 (eV).

MO	SAC/SAC-CI [1]	2ph-TDA [2]	SCF-DSW [3]	DV-Xα [4]	CAS-CI [5]	RESC-CASPT2 [5]	Band
$1t_1$	11.93	12.4	10.422	13.437	9.71	12.40	1
			10.44 (0.02)	13.55 (0.11)		12.43 (0.03)	
$3t_2$	13.14 (1.21)	13.6 (1.2)	10.89 (0.47)	14.126 (0.68)	10.55 (0.84)	13.25 (0.85)	2
			11.21 (0.79)	14.57 (1.13)		13.44 (1.04)	3
$2a_1$	14.54 (2.61)	14.7 (2.3)	12.89 (2.47)	15.86 (2.42)	12.33 (2.62)	14.74 (2.34)	4
$2t_2$	17.85 (5.81)	17.6 (5.2)	14.49 (4.06)	17.55 (4.12)	13.76 (4.05)	17.03 (4.63)	
			14.82 (4.39)	17.75 (4.32)		17.05 (4.65)	5
1e	17.74 (5.70)	18.0 (5.6)	13.67 (3.24)	18.50 (5.06)	14.40 (4.69)	17.17 (4.77)	

[1] Reference[1]
[2] Reference[2]
[3] Reference[3]
[4] Reference[4]
[5] Reference[5]
[6] Reference[6]

Table S2: Empirical estimation of possible values of the asymmetry parameter (β) calculated from Cooper-Zare relation (Equation 6 of the article) and its extension within MO-LCAO framework. The normalized coefficients are from the Hartree-Fock MO coefficients of the concerned MO. Details of the calculation of the β values are given in Equation 7 to 15 of the article and S1 to S18.

MO	Normalized Coefficients				β	
	c_s^2	c_p^2	c_d^2	c_f^2	Direct ionization	Interference
$1t_1$		0.99		0.01	0, 0.99	-0.99
$3t_2$	0.14	0.84	0.02		1.12, 0.28	-0.56
$2a_1$	0.37	0.63			1.37, 0.37	-0.26
$2t_2$	0.10	0.52	0.38		1.02, 0.80, 0.50, 0.30	$0.34, -0.18, 0.01, -0.24, -0.71$
$1e$		0.53	0.47		0.91, 0.62, 0.38, 0.10	$0.06, -0.47, -0.30, -0.44, -1.0$

Table S3: The configuration state functions and the square of the coefficients (weight) contributing to the ground and excited cationic states obtained from (23,14) CASSCF calculations. Only the five most prominent configurations are shown for each state. The calculations were done in the largest Abelian point group (D_2).

$\tilde{X}\ ^2T_1$					$\tilde{A}\ ^2T_2$				
A	B_1	B_2	B_3	Weight	A	B_1	B_2	B_3	Weight
22200	22a	222	222	0.65	22200	2a2	222	222	0.60
2220a	222	22b	22a	0.03	2220a	222	22a	22b	0.04
2220a	222	2a2	22b	0.02	222a0	222	22b	22a	0.03
2220a	222	22b	2a2	0.02	222a0	222	22a	2b2	0.02
222a0	222	2a2	2b2	0.01	22200	a22	222	222	0.01
$\tilde{B}\ ^2A_1$					$\tilde{C}\ ^2T_2$				
A	B_1	B_2	B_3	Weight	A	B_1	B_2	B_3	Weight
a2200	222	222	222	0.53	22200	a22	222	222	0.39
222a0	222	222	220	0.02	222a0	222	2b2	2a2	0.03
2220a	222	222	a2b	0.02	222a0	222	22a	2b2	0.02
222a0	222	222	ab2	0.01	2220a	222	a22	22b	0.02
222a0	222	a2b	222	0.01	a22a0	22b	222	222	0.02
$\tilde{D}\ ^2E$									
A	B_1	B_2	B_3	Weight					
2a200	222	222	222	0.23					
222a0	222	2ba	222	0.06					
222a0	222	222	2ba	0.04					
222a0	222	b2a	222	0.02					
2220a	202	222	222	0.02					

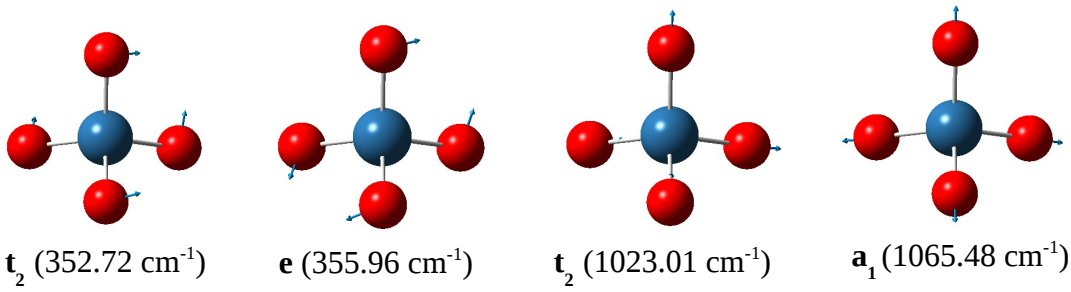

Figure S1: Normal modes of OsO_4.

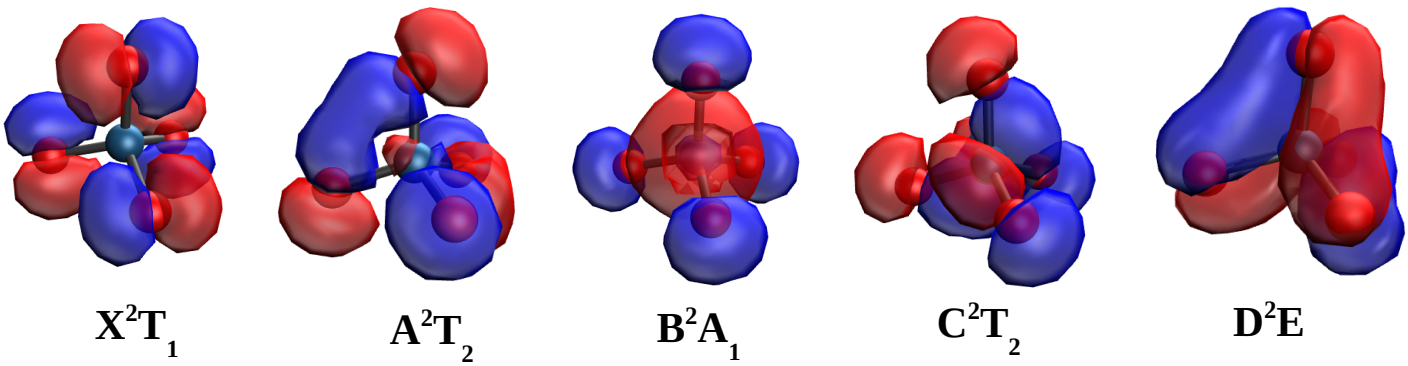

Figure S2: Dyson orbitals associated with the ground and excited states of OsO_4^+ (isovalue = 0.03 a.u.).

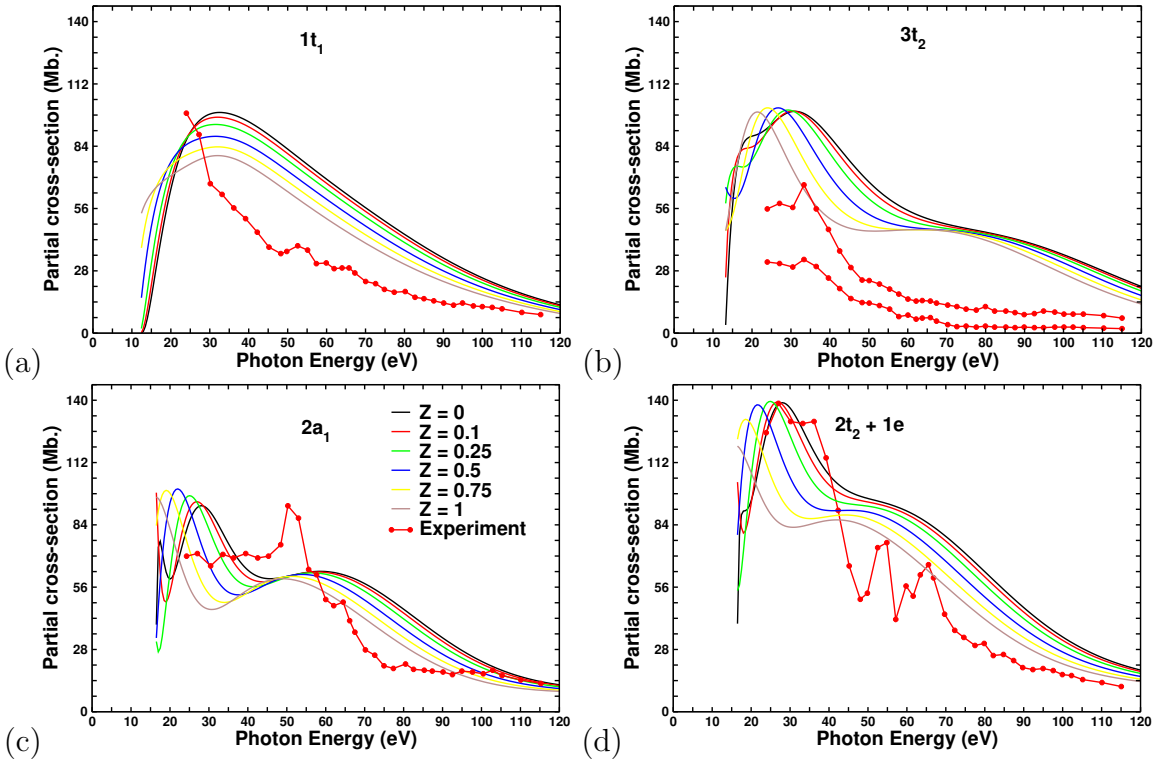

Figure S3: The partial photoionization cross-section corresponding to the ionizations from (a) $1t_1$, (b) $3t_2$, (c) $2a_1$, and (d) $2t_2$ and $1e$ orbitals of OsO_4 by considering different values of the charge of the ionized core (Z) between 0 and 1.0. $Z = 0$ and $Z = 1.0$ represent a plane wave and a Coulomb wave, respectively. The experimental cross section values are reprinted from Reference[2] with permission from Americal Chemical Society. The labels shown in (c) are the same for all figures.

The photoionization cross-sections calculated for different Z values (Figure S3) differ near the threshold region while they are very similar for high photon energies. For $1t^{-1}$ ionization, the partial charge has a marginal role on the position of the peak in the cross section. For $2a_1^{-1}$ ionization, the photon energy corresponding to the maximum cross-section changes noticeably with varying Z. However, all values of Z underestimate the energy of the experimental peak in cross section (Figure S3c). Nevertheless, $Z = 0$ (plane wave) provides the closest agreement to the experimental cross section. The photo-ionization cross sections from $3t_2$ (Figure S3b) and $2t_2 + 1e$ (Figure S3d) ionizations show that the plane-wave description as well as $Z = 0.1$ and $Z = 0.25$, provide reasonable agreement with the experimental cross sections. However, this agreement deteriorates with increasing Z (Figure S3b,d). From this comparison, it can be seen that the overall agreement with the experimental photo-ionization cross section of OsO_4 is better for

smaller values of Z and the plane wave description of the photoelectron provides an even better agreement with the experiment.

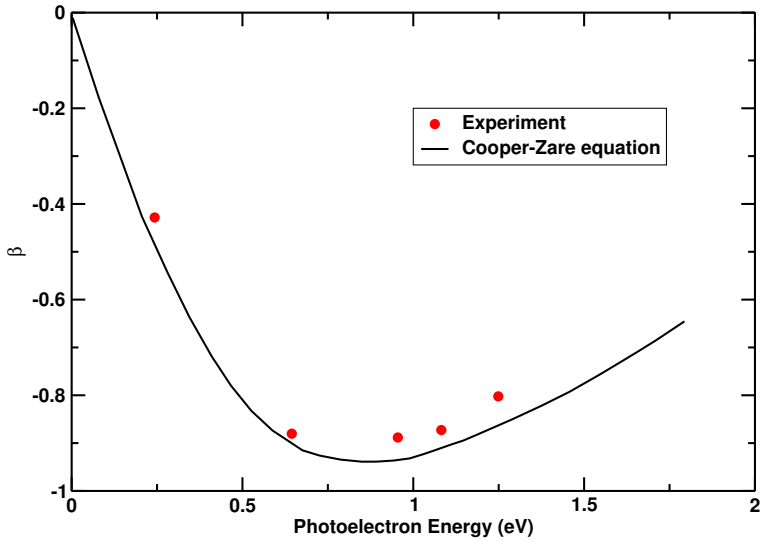

Figure S4: Experimental asymmetry parameter for photodetachment of O^- adapted from Reference.[7] Solid line presents the theoretical results from Cooper-Zare relation.[8]

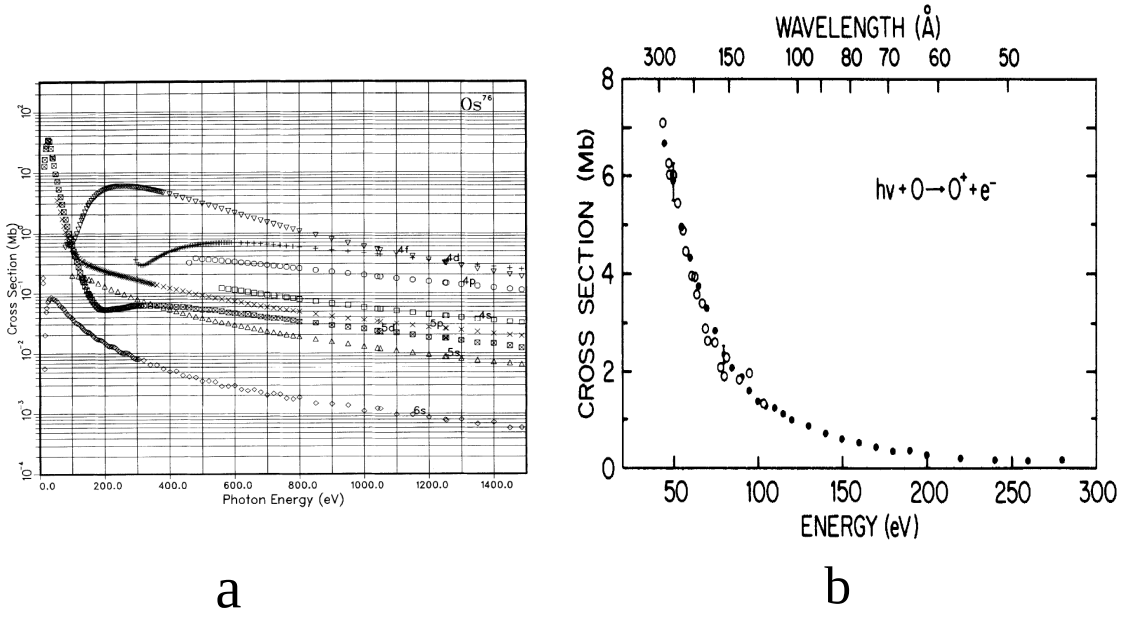

Figure S5: (a) Photoionization cross-section of atomic Os 6s orbital (empty circles), reprinted from Reference[9] with permission from Elsevier. (b) Photoionization cross-section of atomic O, reprinted from Reference[10] with permission from American Physical Society.

Empirical estimation of β for $2t_2^{-1}$ and $1e^{-1}$ ionization

$\mathbf{2t_2^{-1}}$ ionization

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_1^{p\to d} + (0.38)\ \beta_{0.8}^{d\to f} \sim 1.02 \tag{S1}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_1^{p\to d} + (0.38)\ \beta_{0.2}^{d\to p} \sim 0.8 \tag{S2}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_0^{p\to s} + (0.38)\ \beta_{0.8}^{d\to f} \sim 0.50 \tag{S3}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_0^{p\to s} + (0.38)\ \beta_{0.2}^{d\to p} \sim 0.28 \tag{S4}$$

Contribution from inerference terms,

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_1^{p\to d} + (0.38)\ \beta_{-1}^{d\to int.} \sim 0.34 \tag{S5}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_0^{p\to s} + (0.38)\ \beta_{-1}^{d\to int.} \sim -0.18 \tag{S6}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_{-1}^{p\to int.} + (0.38)\ \beta_{0.8}^{d\to f} \sim 0.01 \tag{S7}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_{-1}^{p\to int.} + (0.38)\ \beta_{0.2}^{d\to p} \sim -0.24 \tag{S8}$$

$$\beta_{2t_2} \sim (0.10)\ \beta_2^{s\to p} + (0.52)\ \beta_{-1}^{p\to int.} + (0.38)\ \beta_{0.2}^{d\to int} \sim -0.70 \tag{S9}$$

$\mathbf{1e^{-1}}$ ionization

$$\beta_{1e} \sim (0.53)\ \beta_1^{p\to d} + (0.47)\ \beta_{0.8}^{d\to f} \sim 0.91 \tag{S10}$$

$$\beta_{1e} \sim (0.53)\ \beta_1^{p\to d} + (0.47)\ \beta_{0.2}^{d\to p} \sim 0.62 \tag{S11}$$

$$\beta_{1e} \sim (0.53)\ \beta_0^{p\to s} + (0.47)\ \beta_{0.8}^{d\to f} \sim 0.38 \tag{S12}$$

$$\beta_{1e} \sim (0.53)\ \beta_0^{p\to s} + (0.47)\ \beta_{0.2}^{d\to p} \sim 0.10 \tag{S13}$$

Contribution from the interference terms,

$$\beta_{1e} \sim (0.53)\ \beta_{1}^{p\rightarrow d} + (0.47)\ \beta_{-1}^{d\rightarrow int.} \sim 0.06 \tag{S14}$$

$$\beta_{1e} \sim (0.53)\ \beta_{0}^{p\rightarrow s} + (0.47)\ \beta_{-1}^{d\rightarrow int.} \sim -0.47 \tag{S15}$$

$$\beta_{1e} \sim (0.53)\ \beta_{-1}^{p\rightarrow int.} + (0.47)\ \beta_{0.8}^{d\rightarrow f} \sim -0.30 \tag{S16}$$

$$\beta_{1e} \sim (0.53)\ \beta_{-1}^{p\rightarrow int.} + (0.47)\ \beta_{0.2}^{d\rightarrow p} \sim -0.44 \tag{S17}$$

$$\beta_{1e} \sim (0.53)\ \beta_{-1}^{p\rightarrow int.} + (0.47)\ \beta_{-1}^{d\rightarrow int.} \sim -1.0 \tag{S18}$$

References

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