

Table SI 1: Exoergicities of reaction pathways for the reaction $\text{Ar}^{2+} + \text{O}_2 \rightarrow \text{Ar}^+ + \text{O}_2^+$, calculated from literature values.^{1,2} O_2 is assumed to be in its ground state, $^3\Sigma_g^-$. Highlighted in bold are the pathways with exoergicities between 3 eV and 6.5 eV.

Product states		Reactant (Ar^{2+}) states	Total exoergicity
Ar^+ state, relative to the ground state of Ar, (^1S)	O_2^+ state, relative to the ground state of O_2 , ($^3\Sigma_g^-$)	Ar^{2+} state, relative to the ground state of Ar, (^1S)	Reactant states – total product states
$^2\text{P}^0$, 15.76 eV	$\text{X}^2\Pi_g$, 12.07 eV	^3P , 43.39 eV	15.56 eV
$^2\text{P}^0$, 15.76 eV	$\text{a}^4\Pi_u$, 16.10 eV	^3P , 43.39 eV	11.53 eV
$^2\text{P}^0$, 15.76 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^3P , 43.39 eV	9.46 eV
$^2\text{P}^0$, 15.76 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^3P , 43.39 eV	7.33 eV
$^2\text{P}^0$, 15.76 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^3P, 43.39 eV	3.05 eV
$^2\text{P}^0$, 15.76 eV	$\text{X}^2\Pi_g$, 12.07 eV	^1D , 45.13 eV	17.30 eV
$^2\text{P}^0$, 15.76 eV	$\text{a}^4\Pi_u$, 16.10 eV	^1D , 45.13 eV	13.27 eV
$^2\text{P}^0$, 15.76 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^1D , 45.13 eV	11.20 eV
$^2\text{P}^0$, 15.76 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^1D , 45.13 eV	9.07 eV
$^2\text{P}^0$, 15.76 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^1D, 45.13 eV	4.79 eV
$^2\text{P}^0$, 15.76 eV	$\text{X}^2\Pi_g$, 12.07 eV	^1S , 47.51 eV	19.68 eV
$^2\text{P}^0$, 15.76 eV	$\text{a}^4\Pi_u$, 16.10 eV	^1S , 47.51 eV	15.65 eV
$^2\text{P}^0$, 15.76 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^1S , 47.51 eV	13.58 eV
$^2\text{P}^0$, 15.76 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^1S , 47.51 eV	11.45 eV
$^2\text{P}^0$, 15.76 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^1S , 47.51 eV	7.17 eV
^2S , 29.24 eV	$\text{X}^2\Pi_g$, 12.07 eV	^3P , 43.39 eV	2.08 eV
^2S , 29.24 eV	$\text{a}^4\Pi_u$, 16.10 eV	^3P , 43.39 eV	-1.95 eV
^2S , 29.24 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^3P , 43.39 eV	-4.01 eV
^2S , 29.24 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^3P , 43.39 eV	-6.15 eV
^2S , 29.24 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^3P , 43.39 eV	-10.43 eV
^2S, 29.24 eV	$\text{X}^2\Pi_g$, 12.07 eV	^1D, 45.13 eV	3.82 eV
^2S , 29.24 eV	$\text{a}^4\Pi_u$, 16.10 eV	^1D , 45.13 eV	-0.21 eV
^2S , 29.24 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^1D , 45.13 eV	-2.28 eV
^2S , 29.24 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^1D , 45.13 eV	-4.41 eV
^2S , 29.24 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^1D , 45.13 eV	-8.69 eV
^2S, 29.24 eV	$\text{X}^2\Pi_g$, 12.07 eV	^1S, 47.51 eV	6.2 eV
^2S , 29.24 eV	$\text{a}^4\Pi_u$, 16.10 eV	^1S , 47.51 eV	2.17 eV
^2S , 29.24 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^1S , 47.51 eV	0.10 eV
^2S , 29.24 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^1S , 47.51 eV	-2.03 eV
^2S , 29.24 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^1S , 47.51 eV	-6.31 eV
^4D , 32.17 eV	$\text{X}^2\Pi_g$, 12.07 eV	^3P , 43.39 eV	-0.85 eV
^4D , 32.17 eV	$\text{a}^4\Pi_u$, 16.10 eV	^3P , 43.39 eV	-4.88 eV
^4D , 32.17 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^3P , 43.39 eV	-6.95 eV
^4D , 32.17 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^3P , 43.39 eV	-9.08 eV
^4D , 32.17 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^3P , 43.39 eV	-13.36 eV
^4D , 32.17 eV	$\text{X}^2\Pi_g$, 12.07 eV	^1D , 45.13 eV	0.89 eV
^4D , 32.17 eV	$\text{a}^4\Pi_u$, 16.10 eV	^1D , 45.13 eV	-3.14 eV
^4D , 32.17 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^1D , 45.13 eV	-5.21 eV
^4D , 32.17 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^1D , 45.13 eV	-7.34 eV
^4D , 32.17 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^1D , 45.13 eV	-11.62 eV
^4D, 32.17 eV	$\text{X}^2\Pi_g$, 12.07 eV	^1S, 47.51 eV	3.28 eV
^4D , 32.17 eV	$\text{a}^4\Pi_u$, 16.10 eV	^1S , 47.51 eV	-0.75 eV
^4D , 32.17 eV	$\text{b}^4\Sigma_g^-$, 18.17 eV	^1S , 47.51 eV	-2.83 eV
^4D , 32.17 eV	$\text{B}^2\Sigma_g^-$, 20.30 eV	^1S , 47.51 eV	-4.95 eV
^4D , 32.17 eV	$\text{c}^4\Sigma_u^-$, 24.58 eV	^1S , 47.51 eV	-9.24 eV

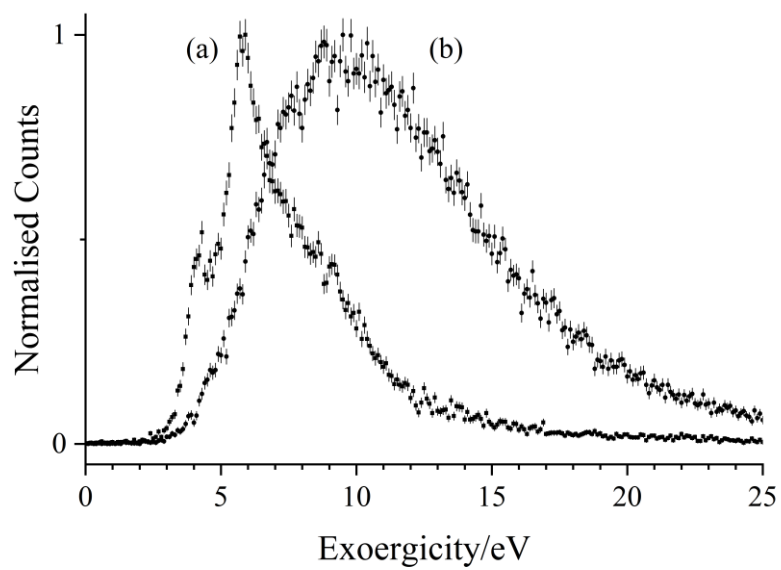


Figure SI 1: Experimental exoergicity spectra for the reaction $\text{Ar}^{2+} + \text{O}_2 \rightarrow \text{Ar}^+ + \text{O}_2^+ \rightarrow \text{Ar}^+ + \text{O}^+ + \text{O}$ with source fields of (a) 28.5 V cm^{-1} and (b) 183 V cm^{-1} . The error bars represent two standard deviations of the counts.