

Electronic Supplementary Material (ESM)

to

**On the Photolysis of simple Anions and neutral Molecules
as Sources of O⁻/ OH, SO_x⁻ and Cl in Aqueous Solution**

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Table S1: Summary of available absolute decadic absorption coefficients from the literature for $\text{SO}_4^{\cdot-}$ in the range of the absorption maximum at $\lambda = 450$ nm.

Authors (Year)	$\epsilon_{10} / \text{l mol}^{-1} \text{cm}^{-1}$	Ref.
Dogliotti and Hayon (1967)	460	[1]
Hayon and McGarvey (1967)	450	[2]
Roebke et al. (1969)	1100	[3]
Chawla and Fessenden (1975)	1600	[4]
McElroy (1990)	1600 ± 100	[5]
Buxton et al. (1990)	1500 ± 50	[6]

Table S2a: Mechanisms for the simulation calculation

Reaction		$k / \text{l mol}^{-1} \text{s}^{-1}$	Ref. k
$\text{HSO}_5^- + h\nu (\lambda = 248 \text{ nm}) \longrightarrow \cdot\text{OH} + \text{SO}_4^{\cdot-}$	(R-28)	---	---
$\cdot\text{OH} + \text{HSO}_5^- \longrightarrow \text{H}_2\text{O} + \text{SO}_5^{\cdot-}$	(R-29)	$1.7 \cdot 10^7$	[7]
$\text{SO}_4^{\cdot-} + \text{HSO}_5^- \longrightarrow \text{HSO}_4^- + \text{SO}_5^{\cdot-}$	(R-30)	$\leq 1 \cdot 10^5$	[8]
$\text{SO}_5^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$	(R-31a)	$1.25 \cdot 10^8$	This work
$\text{SO}_5^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow 2 \text{SO}_4^{\cdot-} + \text{O}_2$	(R-31b)	$5.2 \cdot 10^6$	This work
$\text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-}$	(R-22)	$1.6 \cdot 10^8$	[9]

Table S2b: Applied initial concentrations and absorption coefficients for the simulation calculation.

Species	$c(t=0) / \text{mol l}^{-1}$	$\epsilon (280\text{nm})$ [$\text{l mol}^{-1} \text{cm}^{-1}$]	Reference ϵ
HSO_5^-	$1 \cdot 10^{-3}$	5.2	This work
$\cdot\text{OH}$	$1.24 \cdot 10^{-6}$	235	[10]
$\text{SO}_4^{\cdot-}$	$1.24 \cdot 10^{-6}$	450	This work
$\text{SO}_5^{\cdot-}$	0	559	This work

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Table S3: Results to determine the absolute quantum yields of the SO_4^- formation from the photolysis of HSO_5^- at $\lambda = 248 \text{ nm}$.

Experiment	λ / nm	$A(\text{SO}_4^-)$	$t / \mu\text{s}$	$10^6 \epsilon_t(\text{SO}_4^-)$ mol l^{-1}	$10^6 \epsilon_{t=0}(\text{SO}_4^-)$ mol l^{-1}	$10^{-16} N(\text{SO}_4^-)$	$W_{\text{LASER}} / \text{mJ}$	$10^{-17} N_{\text{ABS}}$	Φ
SO5-50	405	0.185	100	2.16	2.32	3.92	410	3.18	0.123
	425	0.199	100	2.07	2.21	3.74	410	3.18	0.118
	445	0.206	100	2.03	2.17	3.67	410	3.18	0.116
	465	0.198	100	2.06	2.21	3.73	410	3.18	0.117
SO5-51	405	0.188	100	2.20	2.37	4.00	410	3.18	0.126
	425	0.206	100	2.15	2.31	3.89	410	3.18	0.123
	445	0.220	100	2.20	2.37	3.99	410	3.18	0.126
	465	0.191	100	1.98	2.12	3.57	410	3.18	0.112
SO5-52	405	0.177	100	2.06	2.21	3.72	410	3.18	0.117
	425	0.197	100	2.05	2.19	3.69	410	3.18	0.116
	445	0.199	100	1.96	2.09	3.52	410	3.18	0.111
	465	0.192	100	1.99	2.13	3.59	410	3.18	0.113
SO5-53	405	0.182	100	2.12	2.28	3.84	410	3.18	0.121
	425	0.198	100	2.06	2.20	3.71	410	3.18	0.117
	445	0.204	100	2.01	2.15	3.62	410	3.18	0.114
	465	0.184	100	1.90	2.02	3.41	410	3.18	0.108
SO5-54	405	0.182	100	2.12	2.28	3.84	410	3.18	0.121
	425	0.197	100	2.05	2.19	3.69	410	3.18	0.116
	445	0.201	100	1.98	2.11	3.56	410	3.18	0.112
	465	0.183	100	1.89	2.01	3.39	410	3.18	0.107
SO5-42	405	0.237	5	2.86	2.87	4.85	410	3.18	0.153
SO5-43	405	0.233	5	2.81	2.82	4.75	410	3.18	0.150
SO5-44	405	0.223	5	2.67	2.68	4.52	410	3.18	0.142

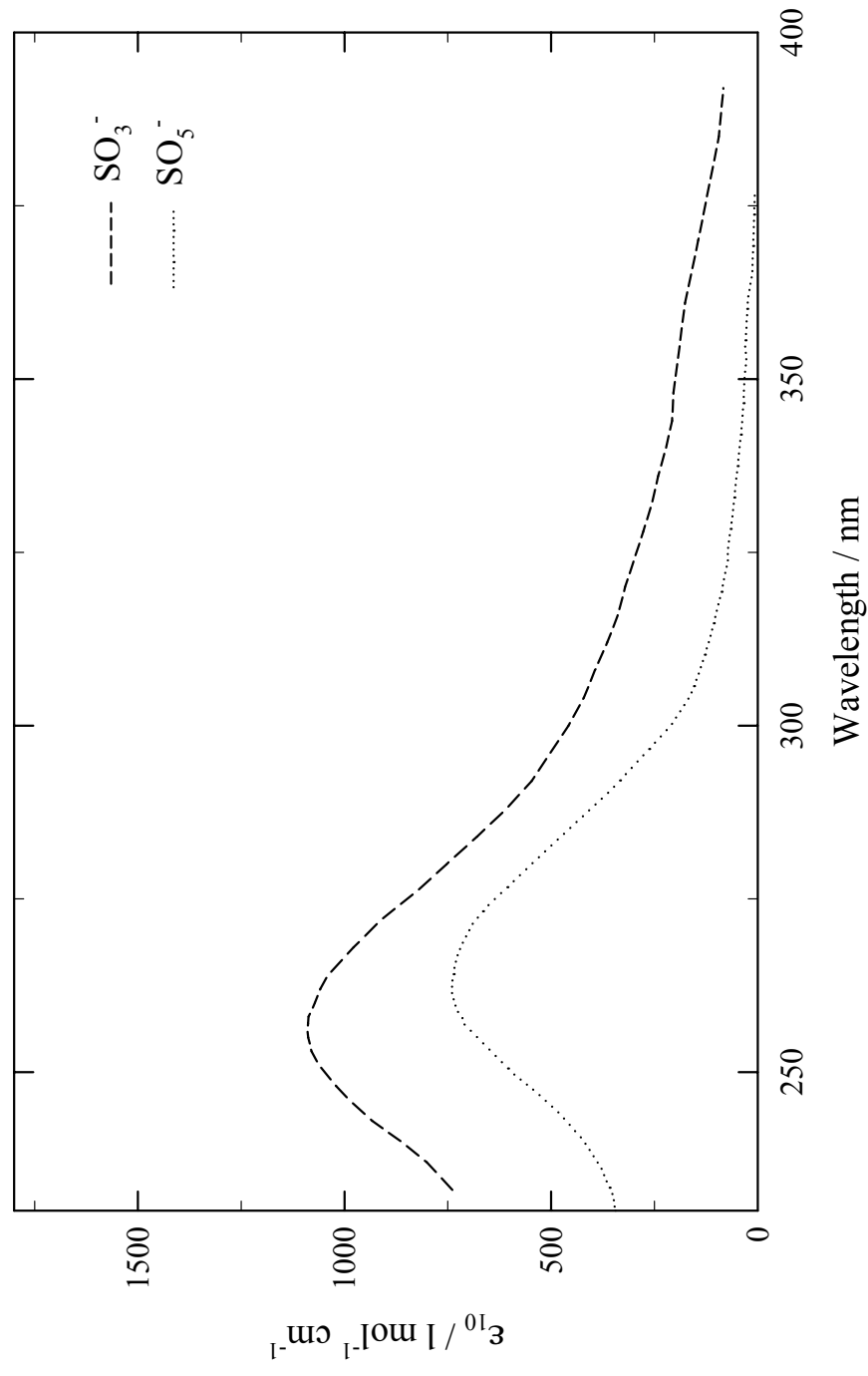


Figure S1: Aqueous phase spectra of SO_3^- and SO_5^- from the photolysis of $\text{S}_2\text{O}_6^{2-}$ at $\lambda = 193 \text{ nm}$ at 298 K .

Table S4: Results to determine the absolute quantum yields of the SO_3^- formation from the photolysis of $\text{S}_2\text{O}_6^{2-}$ at $\lambda = 193$ nm.

Experiment	λ / nm	$\epsilon_{10}(\text{SO}_x^-)$ $\text{l mol}^{-1} \text{cm}^{-1}$	$A(\text{SO}_x^-)$	t / μs	$10^7 c_t(\text{SO}_x^-)$ mol l^{-1}	$10^7 c_{t=0}(\text{SO}_x^-)$ mol l^{-1}	$10^{-16} N(\text{SO}_4^-)$	W_{LASER} / mJ	$10^{-16} N_{\text{ABS}}$	Φ
SO_3^-	240	766	0.034	2.0	3.47	3.47	2.35	100	2.93	0.804
	250	994	0.044	2.0	3.48	3.48	2.36	100	2.93	0.806
	260	1090	0.049	2.0	3.54	3.55	2.40	100	2.93	0.821
	270	989	0.045	2.0	3.59	3.59	2.43	100	2.93	0.831
	280	790	0.036	2.0	3.56	3.56	2.41	100	2.93	0.824
	290	584	0.027	2.0	3.58	3.58	2.43	100	2.93	0.829
	300	437	0.020	2.0	3.55	3.55	2.41	100	2.93	0.822
SO_5^-	240	390	0.016	6.0	3.25	3.25	2.20	100	2.93	0.753
	250	560	0.023	6.0	3.25	3.25	2.20	100	2.93	0.753
	260	726	0.030	6.0	3.30	3.30	2.24	100	2.93	0.764
	270	711	0.030	6.0	3.36	3.36	2.28	100	2.93	0.778
	280	559	0.024	6.0	3.41	3.41	2.31	100	2.93	0.791
	290	360	0.016	6.0	3.45	3.45	2.34	100	2.93	0.800
	300	188	0.008	6.0	3.48	3.48	2.36	100	2.93	0.806

Table S5: Concentrations of the chlorine-containing compounds present in the carried out experiments.

Experiment	Abs.*	$[\text{Cl}_2]/\text{mol l}^{-1}$	$[\text{HOCl}] = [\text{Cl}]/\text{mol l}^{-1}$	$[\text{Cl}_3^-]/\text{mol l}^{-1}$
CL2-1	0.105	$2.0 \cdot 10^{-5}$	$4.6 \cdot 10^{-4}$	$1.8 \cdot 10^{-9}$
CL2-2	0.209	$1.8 \cdot 10^{-5}$	$4.4 \cdot 10^{-4}$	$1.6 \cdot 10^{-9}$
CL2-3	0.060	$2.1 \cdot 10^{-5}$	$4.7 \cdot 10^{-4}$	$1.9 \cdot 10^{-9}$

*: Measured absorption in the mother solution at $\lambda = 325$ nm

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Table S6: Parameter for the evaluation of the quantum yields from the HOCl photolysis in aqueous solution. $\lambda = 248$ nm, $T = 298$ K, $[\text{HOCl}] = 4.4 \cdot 10^{-4}$ mol l⁻¹

λ / nm	A (Cl)	t / ns	$10^7 c_t$ (Cl) mol l ⁻¹	$10^6 c_{t=0}$ (Cl) mol l ⁻¹	$10^{-16} N$ (Cl)	W_{LASER} / mJ	$10^{-16} N_{\text{ABS}}$	Φ
295	0.026	50	7.23	1.24	2.09	290	8.45	0.248
300	0.044	50	7.30	1.25	2.11	290	8.45	0.250
305	0.063	50	7.34	1.27	2.13	290	8.45	0.253
310	0.082	50	7.45	1.28	2.15	290	8.45	0.255
315	0.097	50	7.51	1.29	2.17	290	8.45	0.257
320	0.105	50	7.54	1.29	2.18	290	8.45	0.258
325	0.104	50	7.54	1.29	2.18	290	8.45	0.258
330	0.095	50	7.50	1.29	2.17	290	8.45	0.257
335	0.081	50	7.44	1.28	2.15	290	8.45	0.255
340	0.064	50	7.38	1.27	2.13	290	8.45	0.253
345	0.052	50	7.33	1.26	2.12	290	8.45	0.251
350	0.040	50	7.29	1.25	2.11	290	8.45	0.250
355	0.030	50	7.25	1.24	2.10	290	8.45	0.248
360	0.023	50	7.22	1.24	2.09	290	8.45	0.247
365	0.017	50	7.20	1.24	2.08	290	8.45	0.247

Table S7: Sink reactions for the chlorine atom in the Cl₂/HOCl-system. [HOCl] = [Cl⁻] = 4.4·10⁻⁴ mol l⁻¹

Reaction		k _{2nd} / l mol ⁻¹ s ⁻¹	k _{1st} / s ⁻¹	Ref.
Cl· + Cl· → Cl ₂	(R-42)	1.0·10 ⁸	---	[11]
Cl· + HOCl → HCl + ·OCl	(R-43)	3.0·10 ⁹	1.3·10 ⁶	[11]
Cl· + Cl ⁻ → Cl ₂ · ⁻	(R-44)	2.1·10 ¹⁰	9.2·10 ⁶	[11]
Cl· + H ₂ O → H ⁺ + Cl ⁻ + ·OH	(R-45)	---	2.5·10 ⁵	[5]

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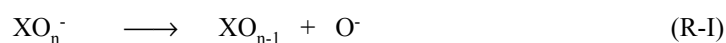
Table S8: Parameter for the evaluation of the quantum yields from the chloroacetone photolysis in aqueous solution. $\lambda = 248$ nm, $T = 298$ K, $[\text{CH}_3\text{COCH}_2\text{Cl}] = 5 \cdot 10^{-4}$ mol l $^{-1}$.

λ / nm	A (Cl)	t / ns	$10^6 c_t$ (Cl) mol l $^{-1}$	$10^6 c_{t=0}$ (Cl) mol l $^{-1}$	10^{-16} N (Cl)	W_{LASER} / mJ	$10^{-17} N_{\text{ABS}}$	Φ
275	0.071	50	0.99	1.02	1.73	290	1.012	0.171
280	0.079	50	1.00	1.03	1.73	290	1.012	0.171
285	0.087	50	1.00	1.03	1.74	290	1.012	0.172
290	0.099	50	1.01	1.04	1.75	290	1.012	0.173
295	0.108	50	1.01	1.04	1.76	290	1.012	0.174
300	0.127	50	1.02	1.06	1.78	290	1.012	0.176
305	0.132	50	1.03	1.06	1.79	290	1.012	0.176
310	0.140	50	1.03	1.06	1.79	290	1.012	0.177
315	0.137	50	1.03	1.06	1.79	290	1.012	0.177
320	0.130	50	1.02	1.06	1.78	290	1.012	0.176
325	0.118	50	1.02	1.05	1.77	290	1.012	0.175
330	0.099	50	1.01	1.04	1.75	290	1.012	0.173
335	0.085	50	1.00	1.03	1.74	290	1.012	0.172
340	0.070	50	0.99	1.02	1.73	290	1.012	0.171
345	0.050	50	0.98	1.01	1.71	290	1.012	0.169
350	0.040	50	0.98	1.01	1.70	290	1.012	0.168
355	0.023	50	0.97	1.00	1.68	290	1.012	0.166

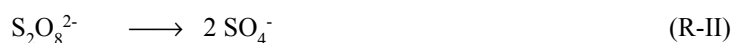
Annex I Thermochemistry of the photodissociation processes in aqueous solution

In order to obtain the excess energies for the different systems, it is necessary to know the bond dissociation energy (BDE) of the X-O⁻ bonds in the precursors molecules.

In the systems where no anions are formed (e.g., H₂O₂, HONO and HOCl), the gas phase BDEs have been considered. For all the other systems where one or both of the fragments are anions the BDEs must be calculated and in the case of the oxy-anions these represent the bond energies of the reaction enthalpies for the reactions:



Whereas for the photolysis of the sulphuroxyl anions,



As well as



The aqueous phase standard enthalpies of formation ($\Delta H_{f(\text{aq})}^0$) for all the treated species are known¹². Furthermore, the gas phase standard enthalpies of formation ($\Delta H_{f(\text{g})}^0$) for all the neutral substrate and products as well as for most of the anions are also existing¹³.

The thermochemistry of several dissociation processes of oxy anions has been discussed with a cyclic process by Friedman¹⁴. This cyclic process is depicted in Figure I.

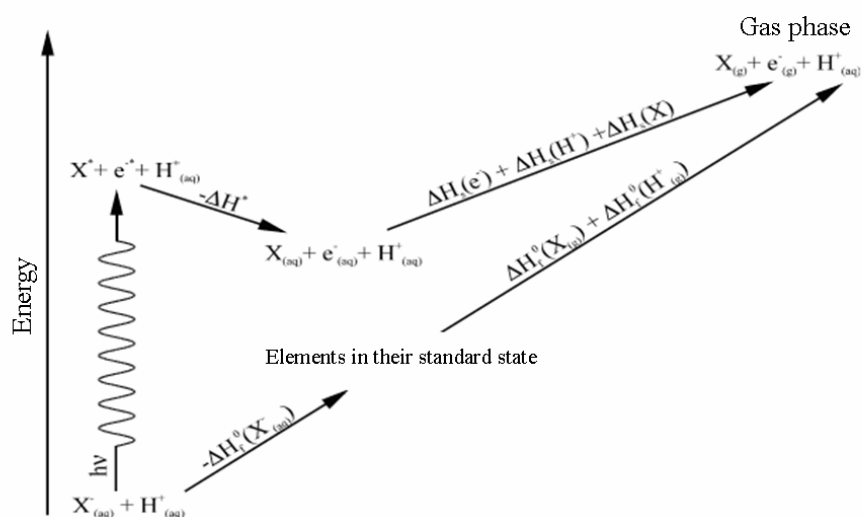
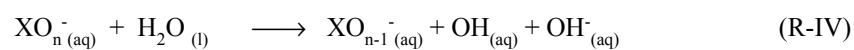


Figure S2: Thermochemistry of the photodissociation of oxy-anions after Friedman¹⁴.

From the thermodynamic treatment after Friedman as well as the following work of Treinin (1970)¹⁵ it follows that the reaction enthalpy (ΔH_R) for the reactions like:



It can be represented and calculated as the sum of R-V:



And the reaction of O^- with the water, e.g.



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However, the reaction enthalpy for the reaction (R-V) can be calculated only for the gas phase since the aqueous phase formation enthalpy ($\Delta H_{f(aq)}^0$) of O^- radical anion is not known. From the gas phase data a value of reaction enthalpy for reaction (R-V) of $\Delta H_R^0(\text{R-V}) = 38.095 \text{ kJ mol}^{-1}$ is given, so that the reaction enthalpy for (R-I) can be calculated as follow:

$$\text{BDE} = \Delta H_R^0(\text{R-I}) = \Delta H_R^0(\text{R-IV}) - \Delta H_R^0(\text{R-V}) \quad (\text{I})$$

Whereas the Treinin values have been considered for the reaction enthalpy of the reactions like (R-IV)¹⁵. The obtained values have been summarised in Table IX.

The gas phase BDEs have been applied for in the case of HOX with X= OH, Cl, NO.

For the peroxy energy bond in the peroxomonosulphate anion (HSO_5^-) the value of $\text{BDE} = 377 \text{ kJ mol}^{-1}$ given by Benson¹⁶ has been considered. A BDE of 92 kJ mol^{-1} is given for the peroxy bond in the $\text{H}_2\text{S}_2\text{O}_8$ molecule, which has been also applied for the peroxodisulphate anion. A thermochemical calculation for this bond leads to a BDE ($\text{O}_3\text{S-OO-SO}_3^-$) = 93 kJ mol^{-1} , in which the standard entropy of formation ΔS_f^0 has been assumed equivalent to the one of the sulphate radical anion (SO_4^-) ($\Delta S_f^0(\text{SO}_4^{2-}) = 20.8 \text{ J mol}^{-1} \text{ K}^{-1}$ ¹²). The good agreement obtained with the Benson value shows the validity of the taken approximation.

No BDE is available for the S-S bond in the dithionate anion, therefore an estimation have been done. The Gibbs free energy of of formation (ΔG_f^0) for $\text{S}_2\text{O}_6^{2-}$ and SO_3^- are $\Delta G_f^0(\text{S}_2\text{O}_6^{2-}) = -960 \text{ kJ mol}^{-1}$ ¹² and $\Delta G_f^0(\text{SO}_3^-) = -426 \text{ kJ mol}^{-1}$, respectively¹². A similar approximation to the case of sulphate radical anion has been taken and a $\Delta S_f^0(\text{SO}_3^{2-}) = \Delta S_f^0(\text{SO}_3^-) = -293 \text{ J mol}^{-1} \text{ K}^{-1}$ ¹² have been applied. The aqueous phase ΔS_f^0 of dithionate anion is also not known and it has been estimated equal to $\Delta S_f^0(\text{S}_2\text{O}_6^{2-}) = 160 \text{ J mol}^{-1} \text{ K}^{-1}$ as average value between $\text{S}_2\text{O}_4^{2-}$ and $\text{S}_2\text{O}_8^{2-}$ values¹². Applying the Gibbs-Helmholtz relationship, the bond dissociation energy of S-S bond in the dithionate anion has been calculated as follow:

$$\text{BDE}(\text{O}_3\text{S-SO}_3^-) = 2 \cdot \Delta G_f^0(\text{SO}_3^-) - \Delta G_f^0(\text{S}_2\text{O}_6^{2-}) - \frac{298}{1000} \cdot (2 \cdot \Delta S_f^0(\text{SO}_3^-) - \Delta S_f^0(\text{S}_2\text{O}_6^{2-})) \quad (\text{II})$$

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It follows a value of BDE ($\text{O}_3\text{S-SO}_3^-$) = 173 kJ mol⁻¹. This results is in good agreement with suggestion of Waygood und McElroy, whose indicated that the BDE of the S-S-bond in $\text{S}_2\text{O}_6^{2-}$ should be double respect to the BDE of the peroxy bond in $\text{S}_2\text{O}_8^{2-}$ ¹⁷.

Table S9: Applied bond dissociation energies (BDEs, kJ mol⁻¹)

Precursor XO_n^-	BDE($\text{XO}_{n-1}\text{-O}^-$) /kJ mol⁻¹	Measurement / Ref.
NO_2^-	192	This work, see text
NO_3^-	217	This work, see text
ClO^-	230	This work, see text
ClO_2^-	150	This work, see text
Precursor XOH	BDE(X-OH) /kJ mol⁻¹	Measurement / Ref.
H_2O_2	213 ± 4	Gas phase, [12]
HOCl	251 ± 13	Gas phase, [12]
HONO	206	Gas phase, [12]
HSO_5^-	377	Benson, [16]
Precursor [XO_n^-]₂	BDE(XO_n^--XO_n^-) /kJ mol⁻¹	Measurement / Ref.
$\text{S}_2\text{O}_8^{2-}$	92	Benson, [16]
$\text{S}_2\text{O}_6^{2-}$	173	This work, see text

From the obtained BDEs the total excess energy can then be calculated as:

$$W_{\text{exc}} = W(\text{h}\nu) - \text{BDE} \text{ [kJ mol}^{-1}\text{]} \quad (\text{III})$$

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