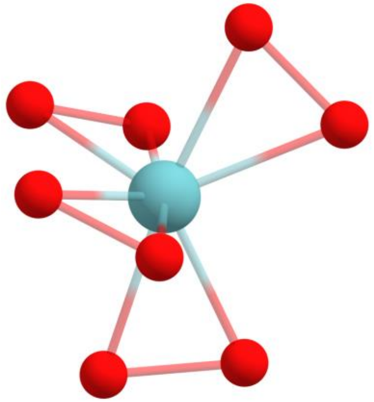
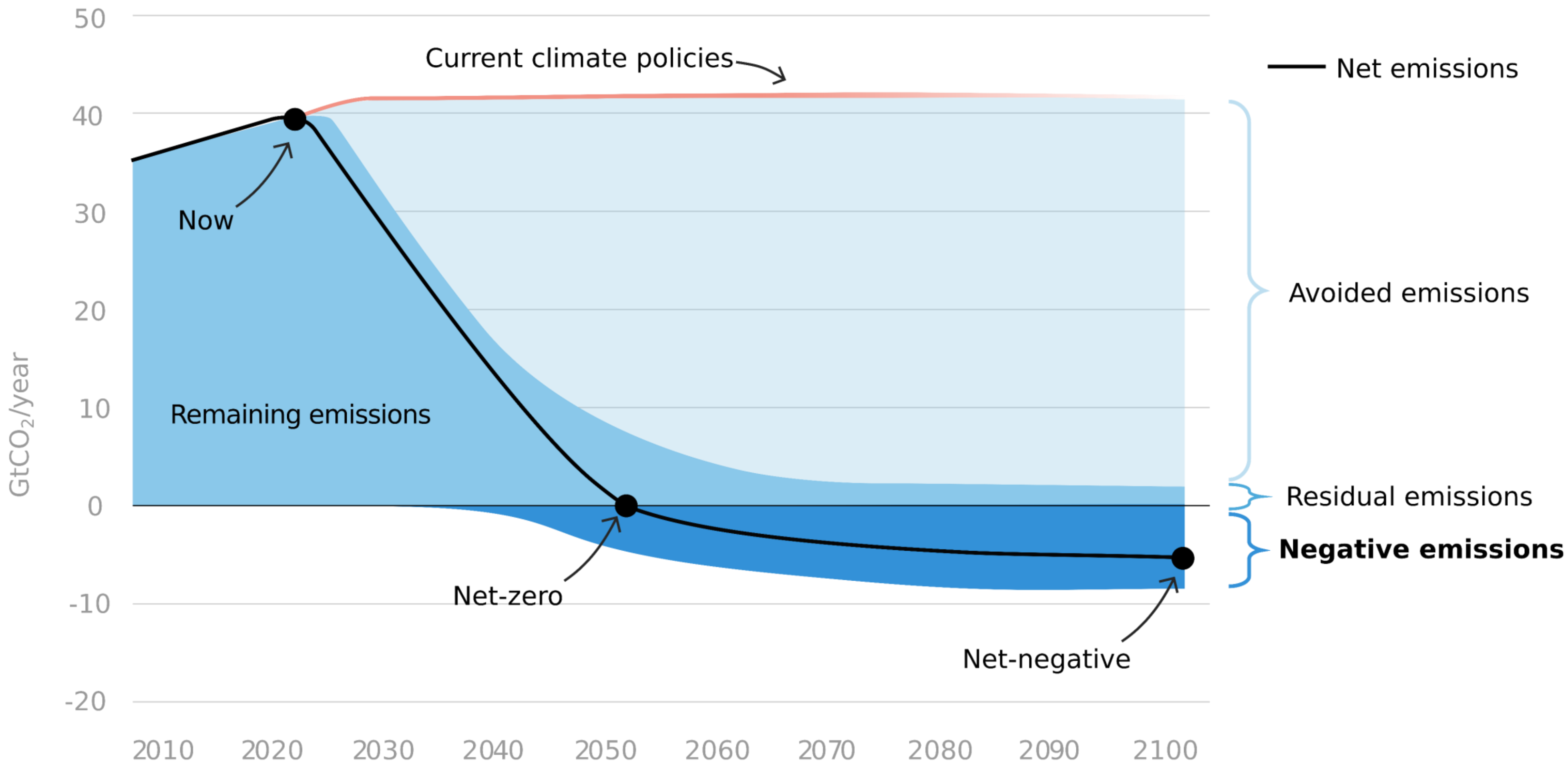
Electronic Structure and CO_2 Reactivity of Group IV/V/VI Tetraperoxometalates



Jacob Hirschi
Advisor: Prof. Tim Zuehlsdorff
August 18, 2024

Oregon State University

1.5°C Warming Scenario



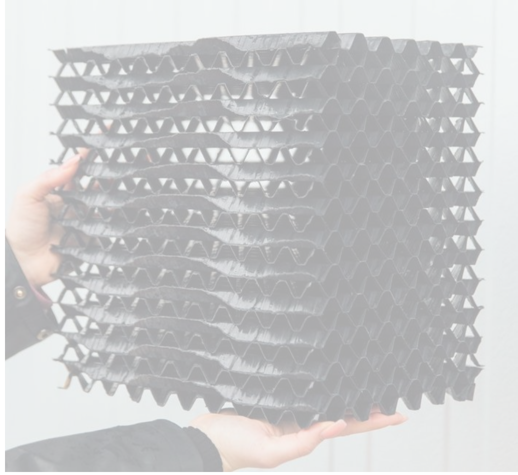
Direct Air Capture (DAC) Costs

Economies of scale

Present: \$600 – 1,000/t-CO_2

DOE Target: \$**100**/t-CO_2

Engineering



Direct Air Capture (DAC) Costs

Economies of scale

Present: \$600 – 1,000/t-CO_2

DOE Target: \$**100**/t-CO_2

Engineering

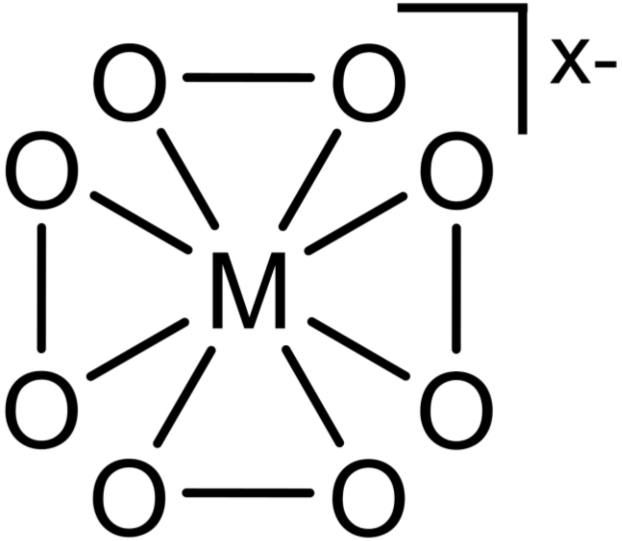
Tetraperoxometalates

Prof. May Nyman

Four O_2^{2-} ligands

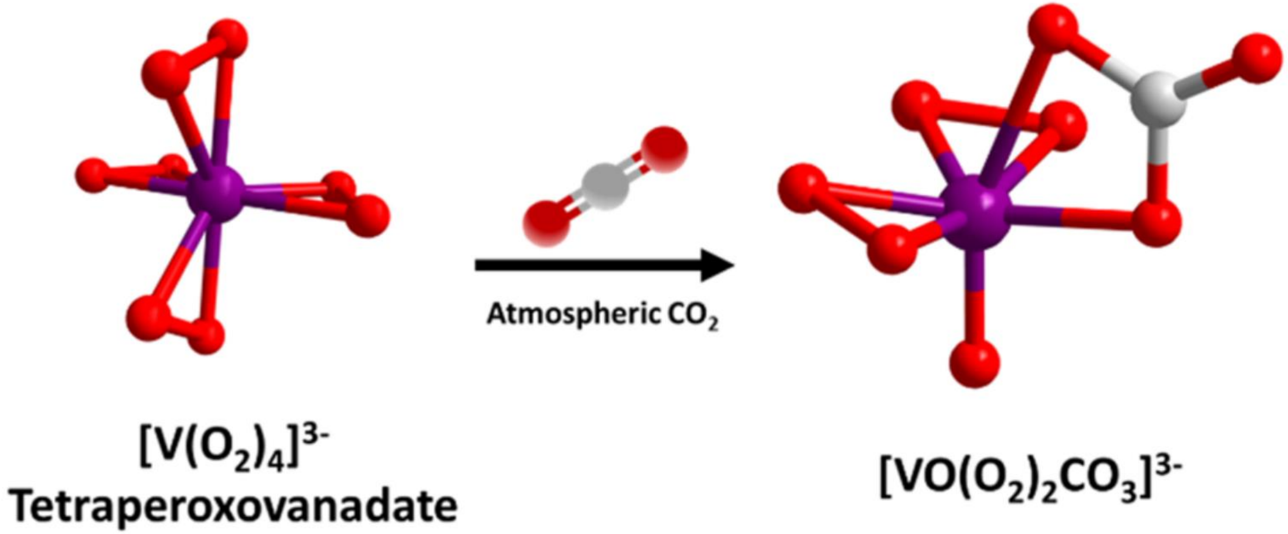
d^0 transition metal, M

Anionic, x-



$[V(O_2)_4]^{3-}$
Tetraperoxovanadate

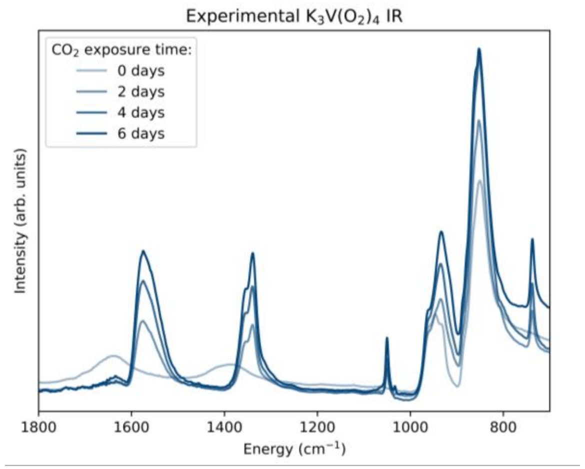
DAC with $(Cs/\underline{K}/Na)_3\underline{V}(O_2)_4$



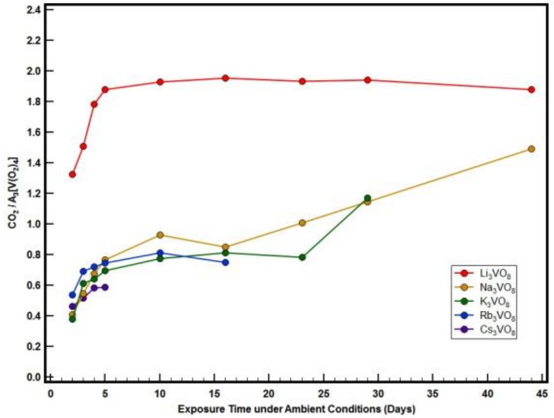
> 1 month exposure

Ribó, E. G.; et al. *Chem. Sci.* **2024**, *15*, 1700.

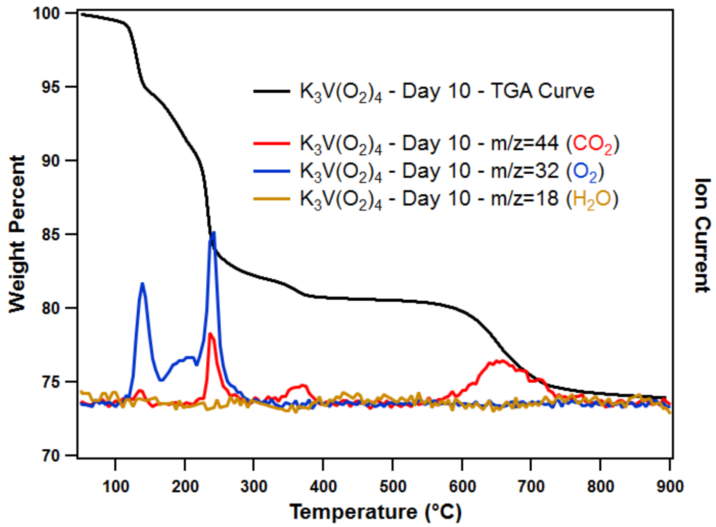
Experimental Characterization



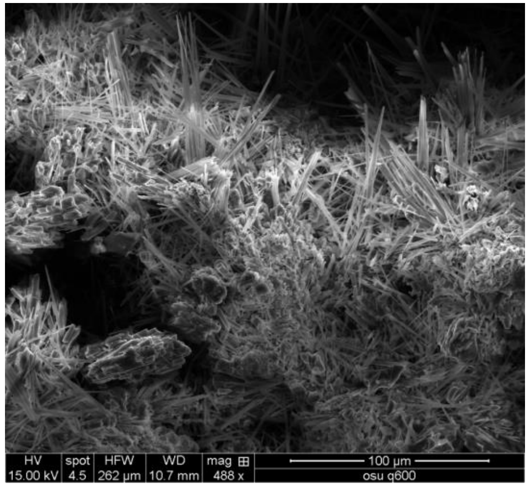
IR/Raman Spectra



CHN Analysis



TGA-MS



$Na_3[V(O_2)_4]$ + 4 months exposure

SEM Images

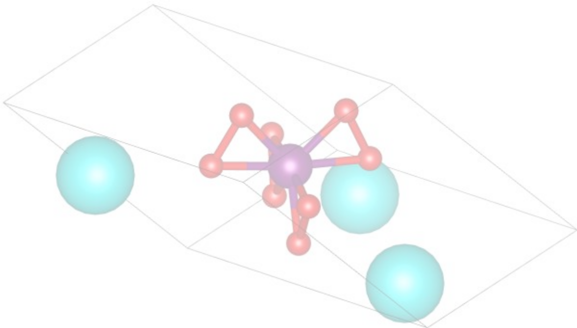
DFT Modelling

Experiment

Solid $K_3V(O_2)_4$

Simulation

Solid-state

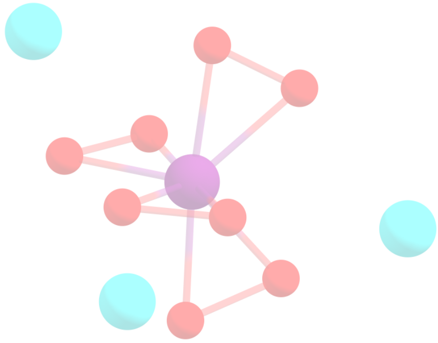


CASTEP

PBE
850 eV
2x2x2 k-grid

VS

Cluster-model



CAM-B3LYP
LANL2DZ/6-31+G*

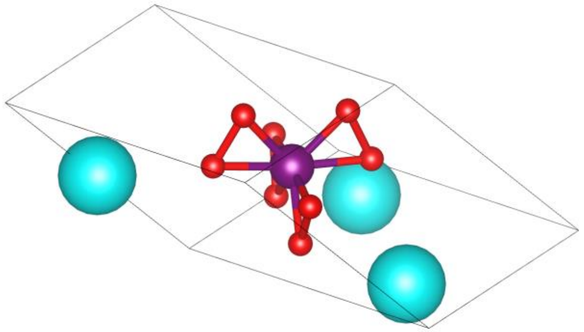
DFT Modelling

Experiment

Solid $K_3V(O_2)_4$

Simulation

Solid-state



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PBE
850 eV
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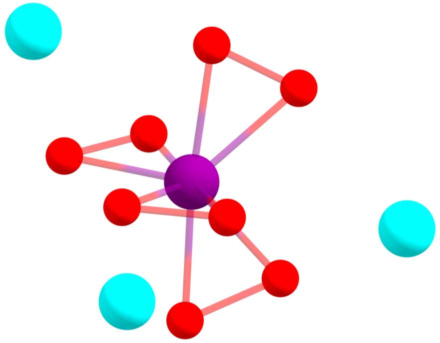


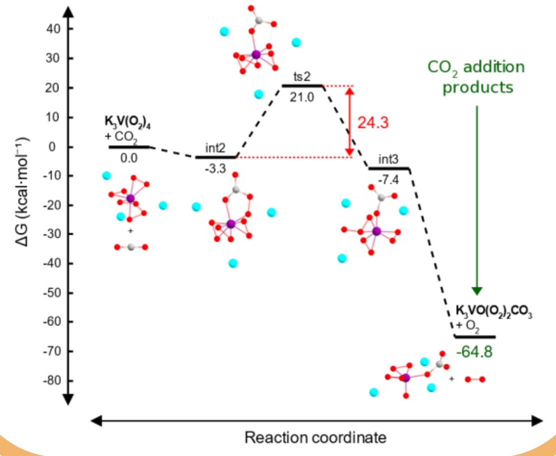
CAM-B3LYP
LANL2DZ/6-31+G*

castep.org gaussian.com

DAC with $K_3V(O_2)_4$

Computations

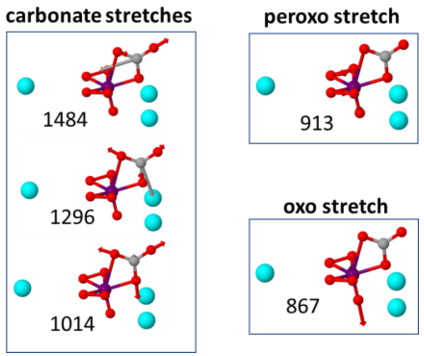
Mechanism



Solid-state Thermo.

Reaction	$\Delta G_{298\ K}$ (kcal/mol)
$K_3V(O_2)_4 + CO_2 \rightarrow K_3VO(O_2)_2CO_3 + O_2$	-52.1
$K_3VO(O_2)_2CO_3 + CO_2 \rightarrow K_3VO_2(CO_3)_2 + O_2$	-29.5
$K_3V(O_2)_4 + 2CO_2 + H_2O \rightarrow KVO_3 + 2KHCO_3 + O_2$	-92.8
$K_3V(O_2)_4 + H_2O \rightarrow KVO_3 + 2KOH + 2O_2$	-58.2
$K_3VO(O_2)_2CO_3 \rightarrow K_3VO_4 + CO_2 + O_2$	-14.5

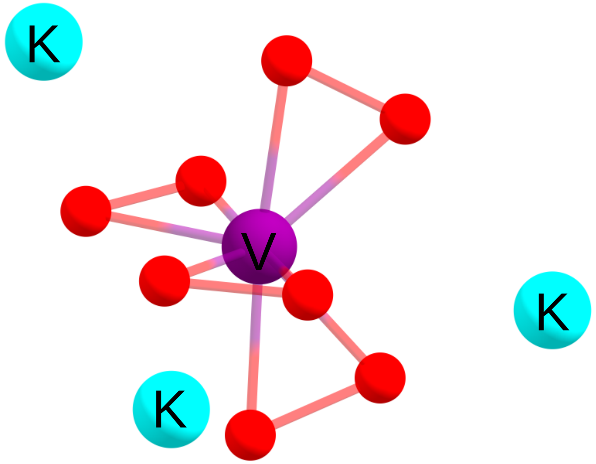
Phonons

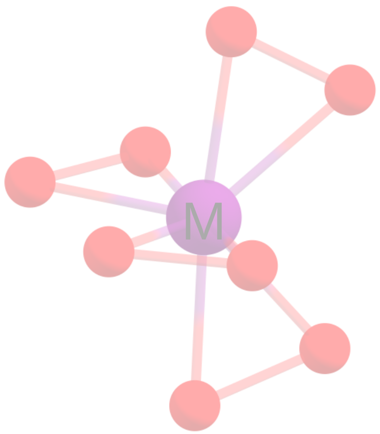


Can We Improve the Material?

$K_3V(O_2)_4$ in vacuum

$[M(O_2)_4]^{x-}$ in PCM:water





Metal Center, **M** =

Ti, **V**, Cr

Zr, Nb, Mo

Hf, Ta, W

Can We Improve the Material?

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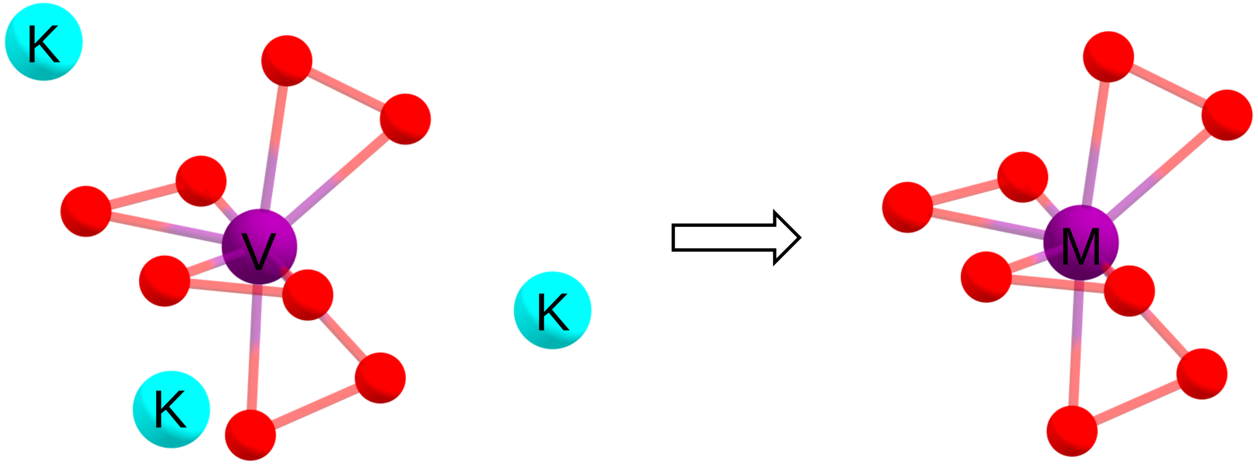


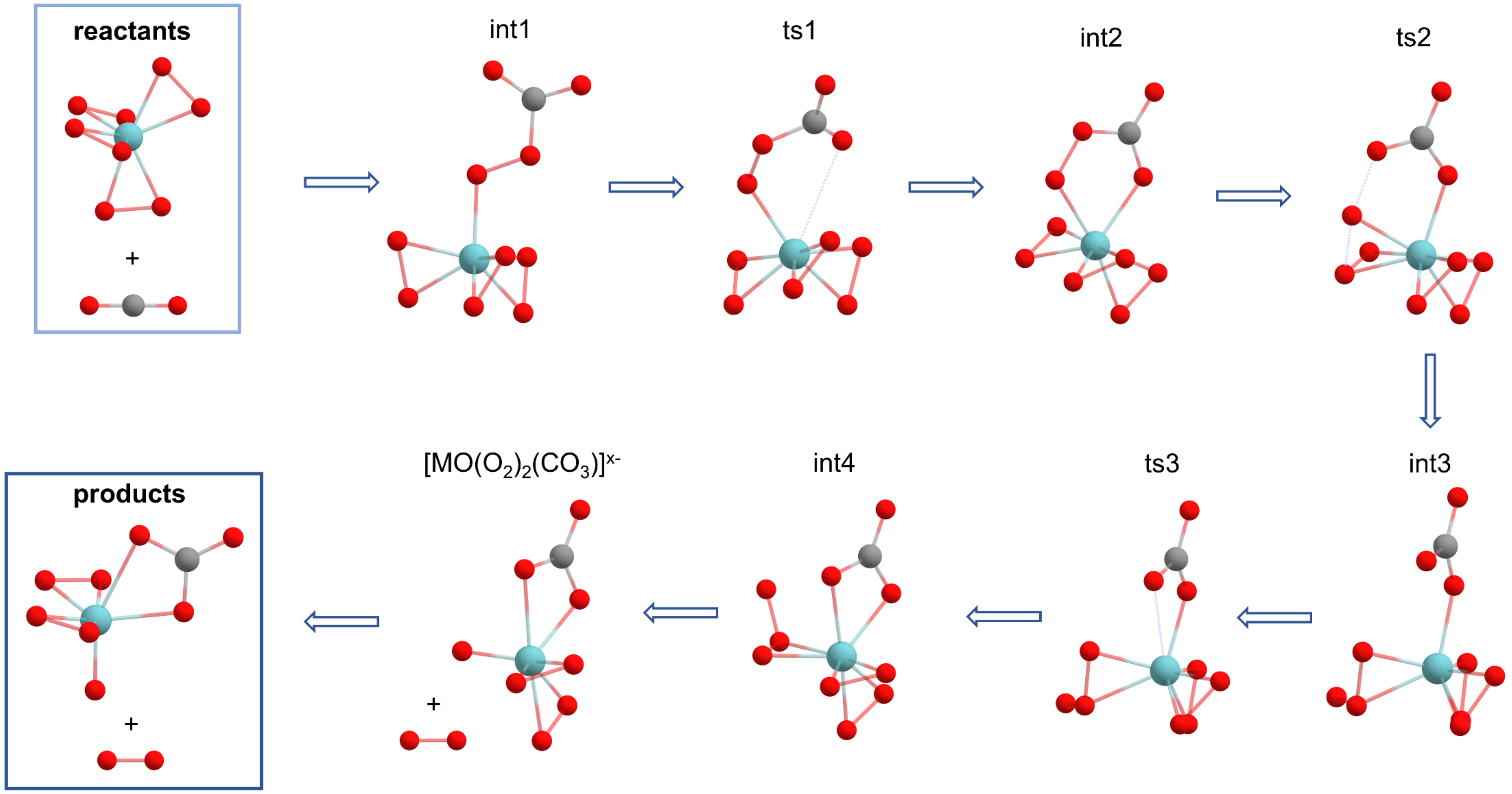
Metal Center, **M** =

Ti, **V**, Cr

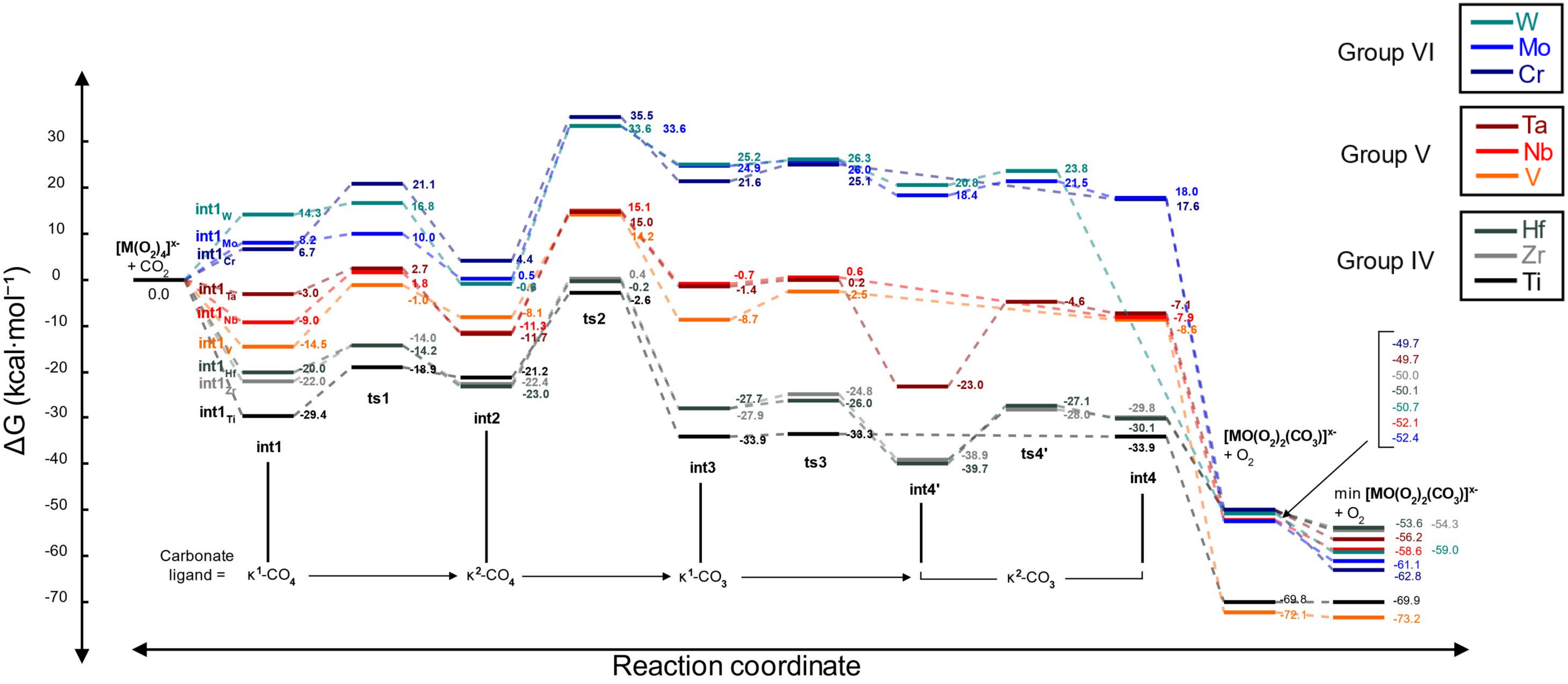
Zr, Nb, Mo

Hf, Ta, W

Reaction Mechanism

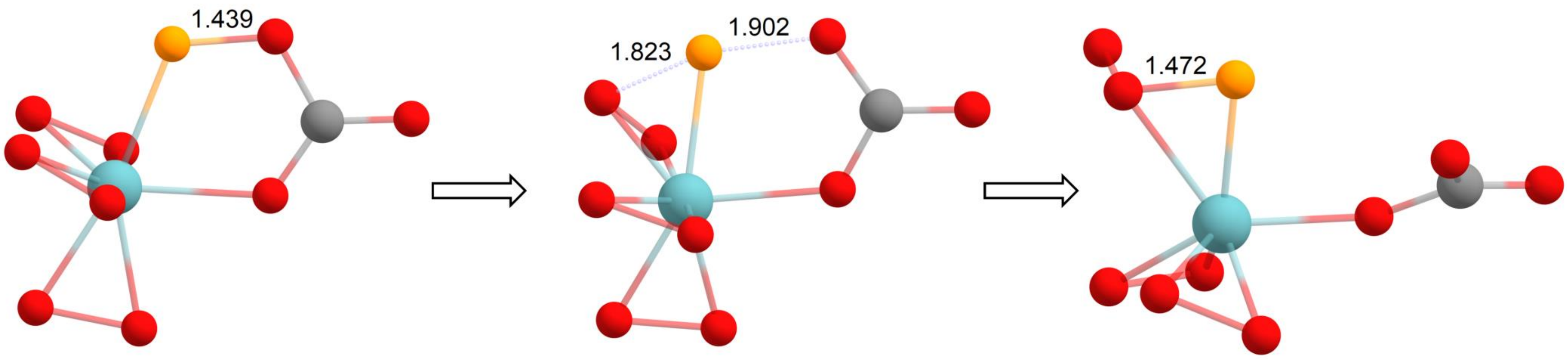


Reaction Mechanism



Rate-Determining (RD) Step

Oxygen atom transfer



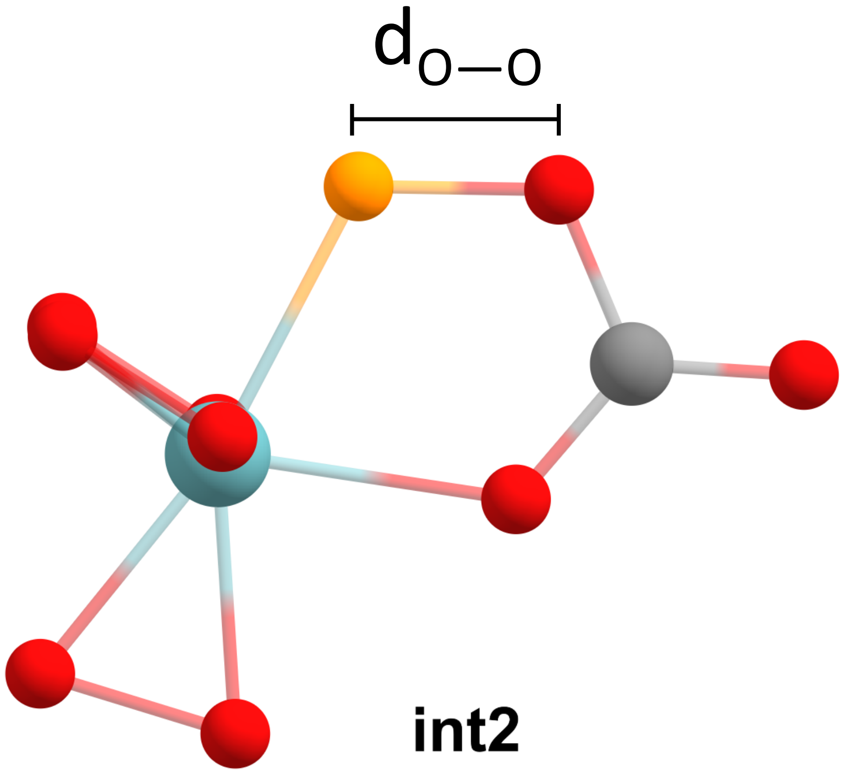
int2 ts2 int3

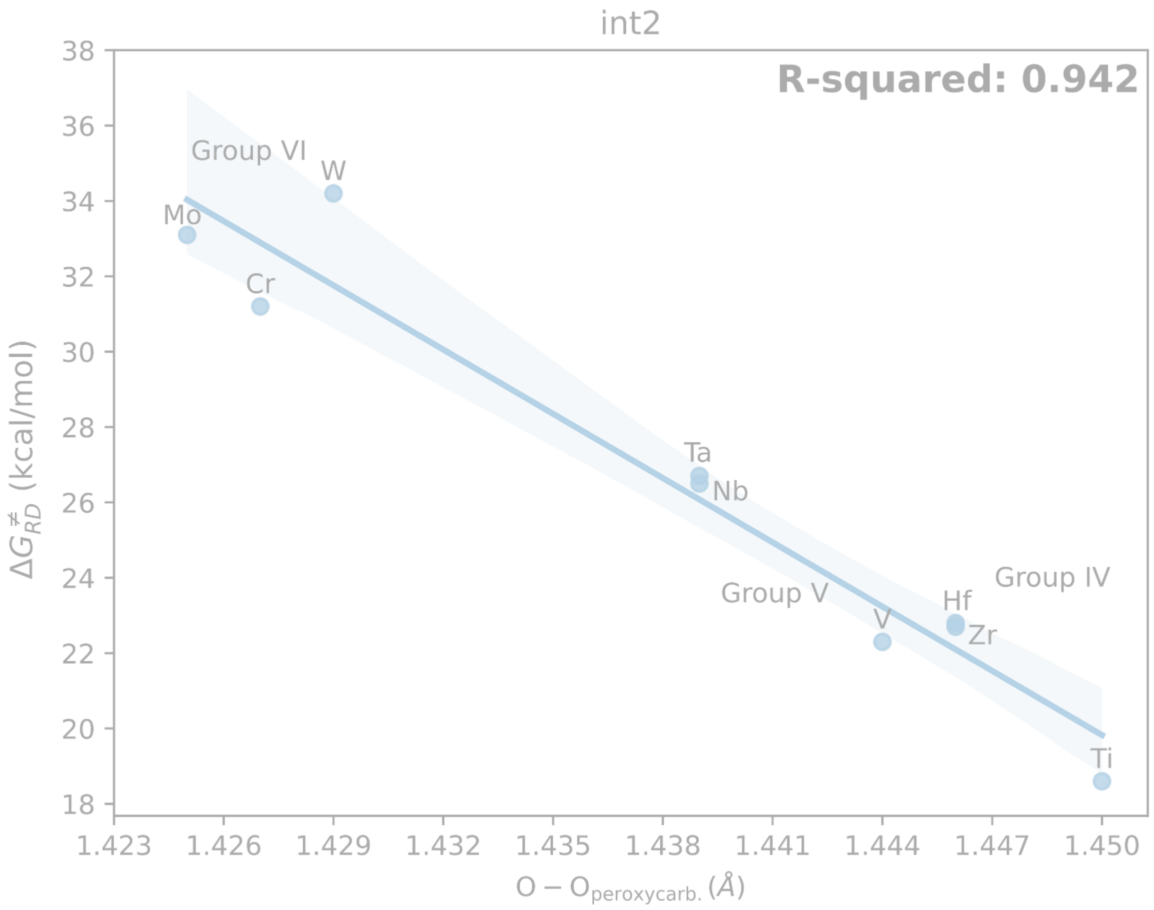
Rate-Determining (RD) Step

M $\Delta G^{\neq}$ (kcal/mol) =

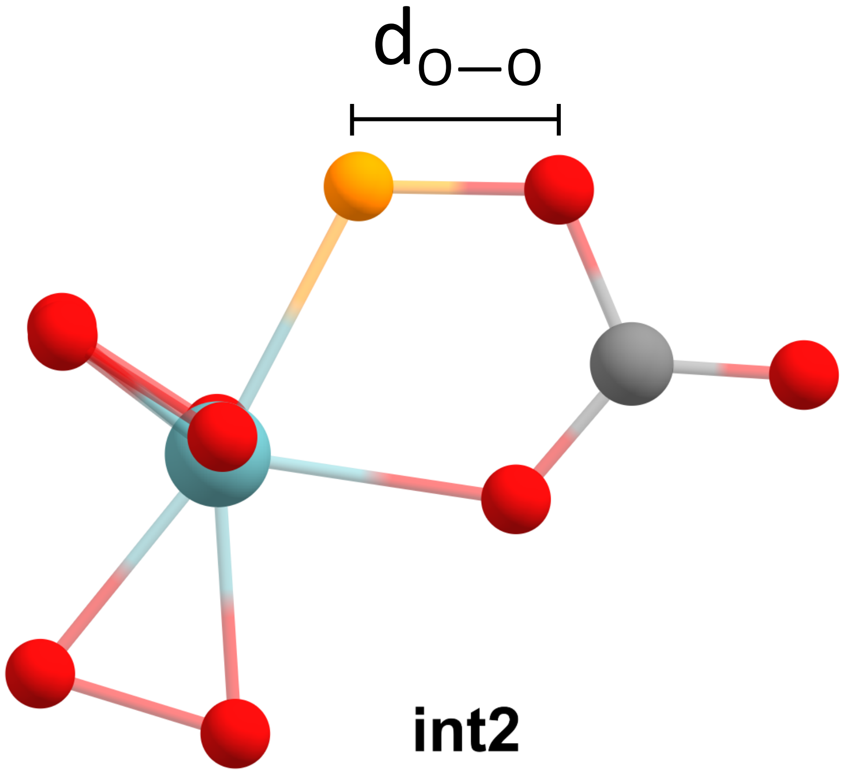
IV	V	VI
Ti 18.6	**V** 22.3	**Cr** 31.2
Zr 22.8	**Nb** 26.5	**Mo** 33.1
Hf 22.7	**Ta** 26.7	**W** 34.2

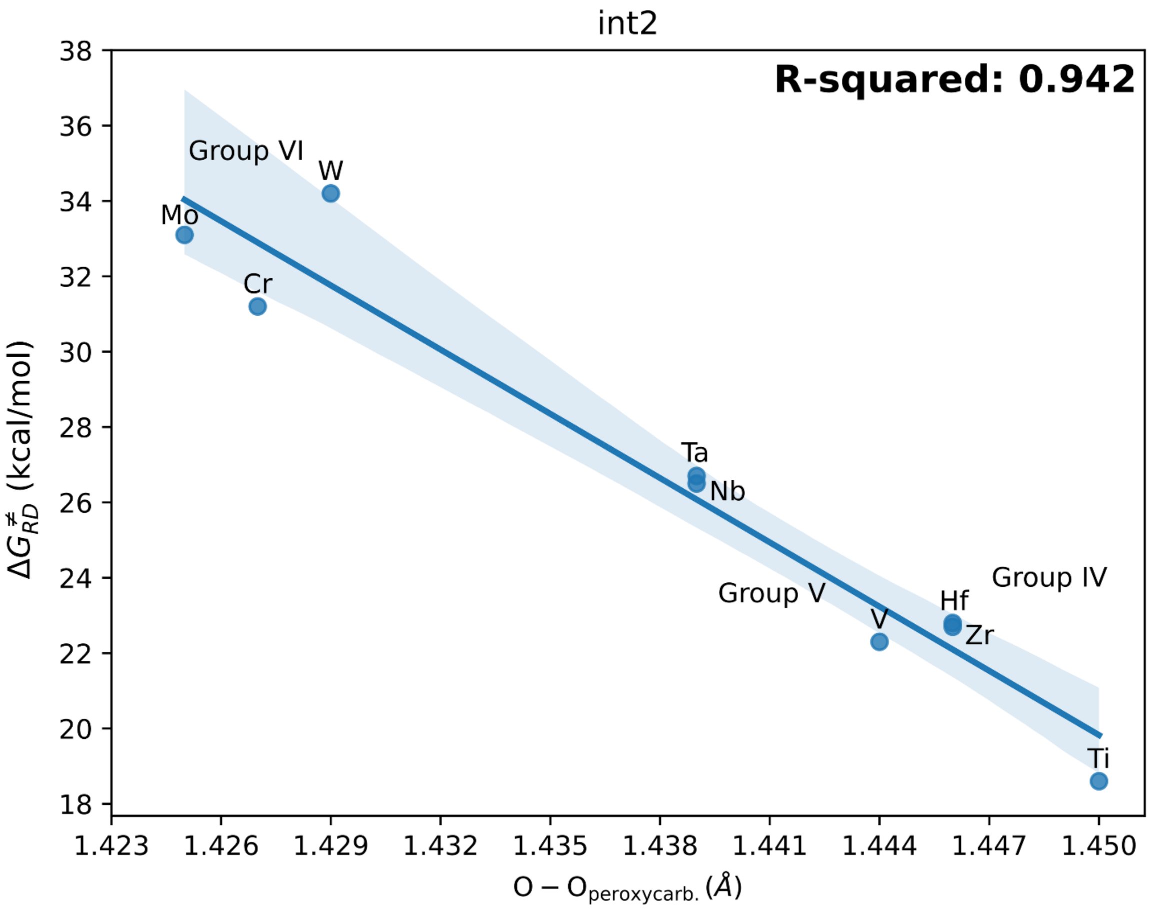
RD Step Trends 1





RD Step Trends 1



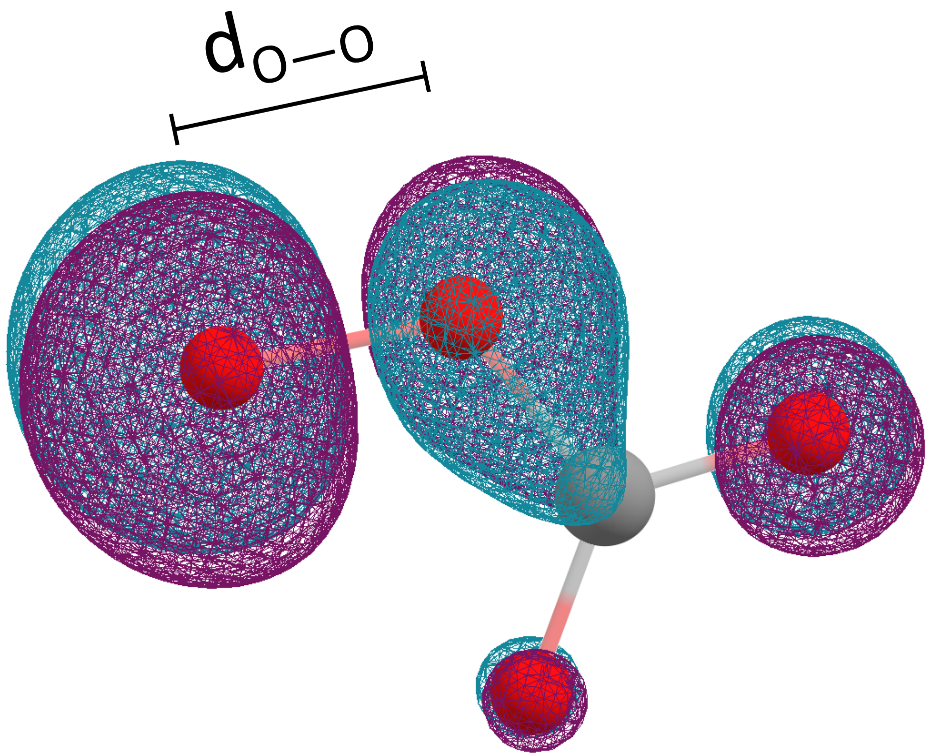


Peroxycarbonate, CO_4^{2-}

$\pi^*(O-O)$ Orbital

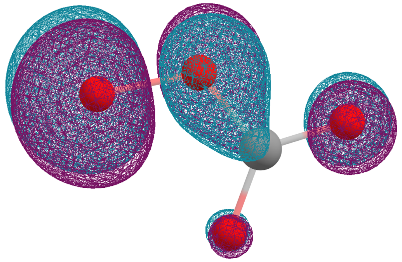
E(HOMO) = -6.26 eV

d_{O-O} = 1.456 Å



$\pi^*(O - O)$ Orbital

free ligand

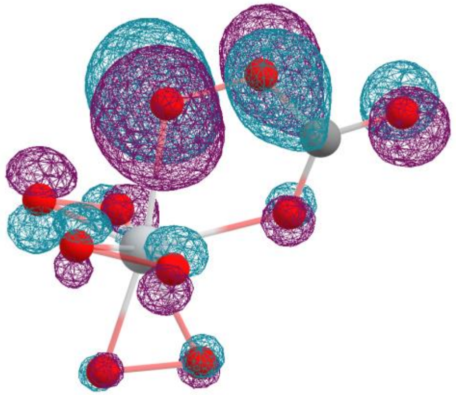


CO_4^{2-}

-6.26 eV

1.456 Å

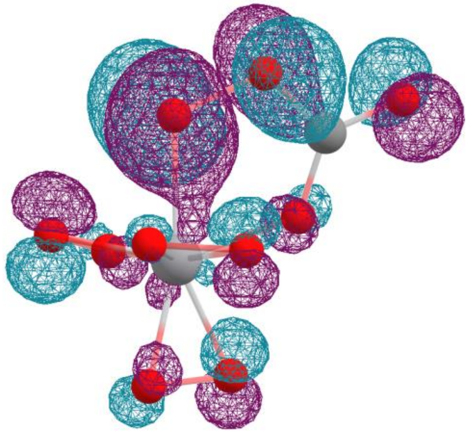
int2



Ti

-6.50 eV

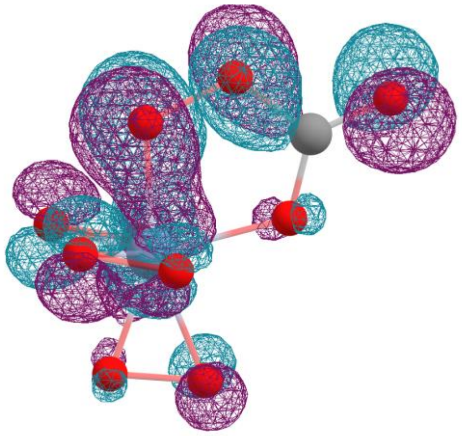
1.450 Å



V

-7.26 eV

1.444 Å

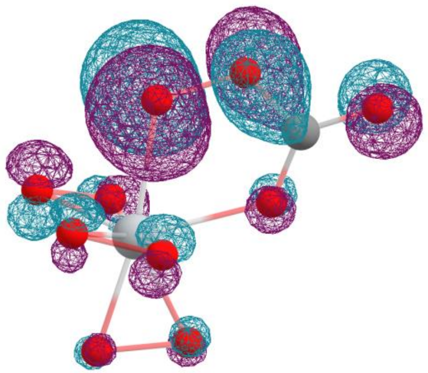


Cr

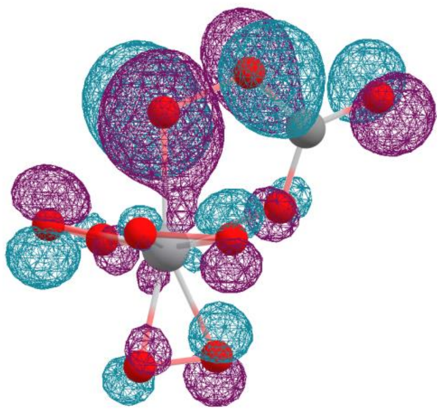
-8.50 eV

1.427 Å

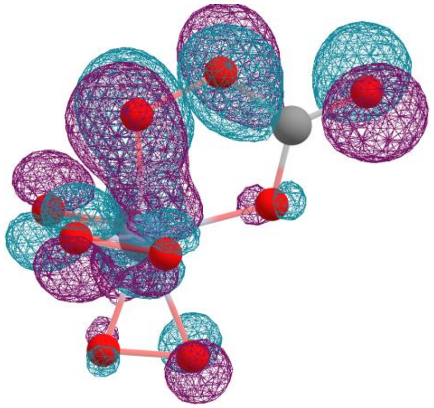
RD Step Trends 2



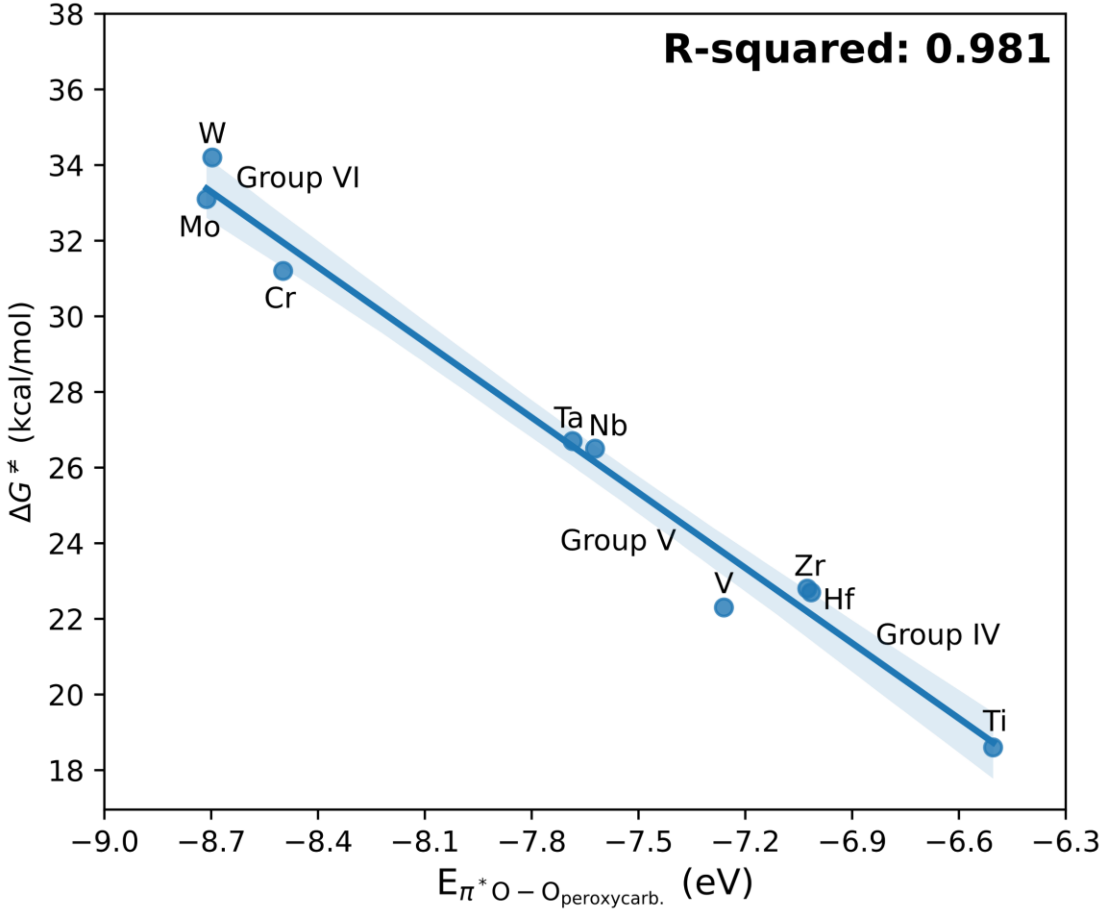
Ti, -6.50 eV



V, -7.26 eV



Cr, -8.50 eV

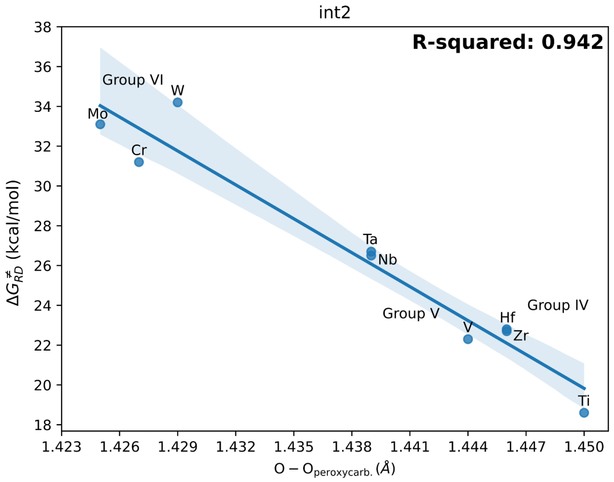


RD Step Trends

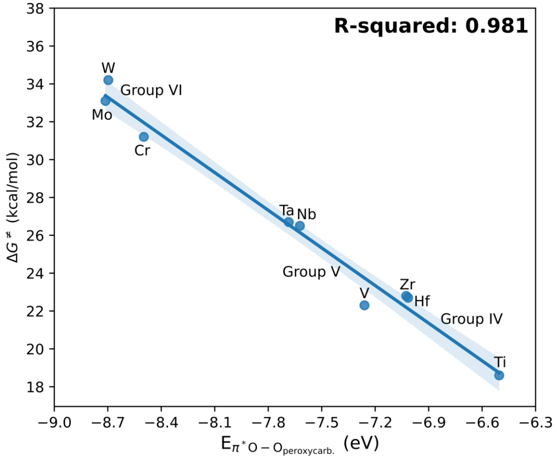
M $\Delta G^{\neq}$ (kcal/mol) =

IV	V	VI
Ti 18.6	**V** 22.3	**Cr** 31.2
Zr 22.8	**Nb** 26.5	**Mo** 33.1
Hf 22.7	**Ta** 26.7	**W** 34.2

d_{O-O} Bond



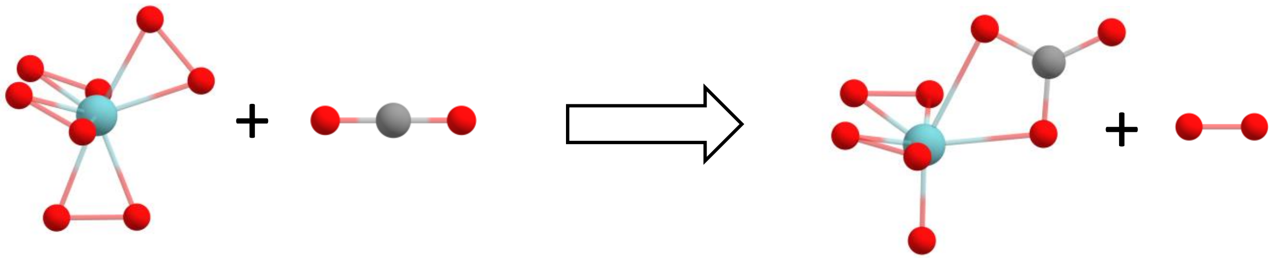
$\pi^*(O-O)$ Orbital



Material Degradation

$[M(O_2)_4]^{x-} + CO_2 \rightarrow [MO(O_2)_2(CO_3)]^{x-} + O_2$

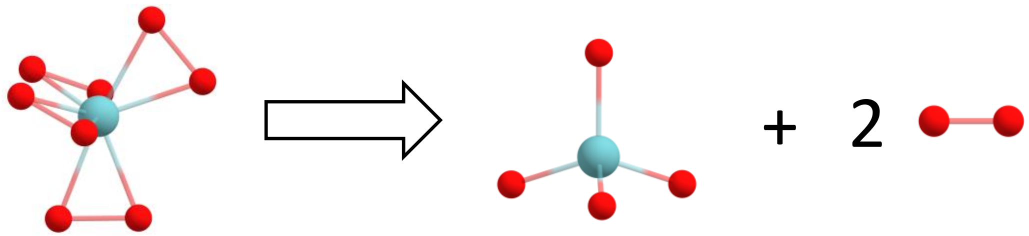
Carbon Capture



vs

$[M(O_2)_4]^{x-} \rightarrow [MO_4]^{x-} + 2O_2$

Decomposition



Material Degradation

Carbon Capture

vs

Decomposition

M	$\Delta G_{CO_2 \text{ cap.}}$ (kcal/mol)	$\Delta G_{\text{decomp.}}$ (kcal/mol)	$\frac{\Delta G_{CO_2 \text{ cap.}}}{\Delta G_{\text{decomp.}}}$
Ti	-69.9	-39.2	1.78
Zr	-54.3	-10.9	4.98
Hf	-53.6	-12.9	4.16
V	-73.2	-82.3	0.89
Nb	-58.6	-55.2	1.06
Ta	-56.2	-53.7	1.05
Cr	-62.8	-114.4	0.55
Mo	-61.1	-104.0	0.59
W	-59.0	-102.4	0.58

Material Degradation

Carbon Capture

vs

Decomposition

M	$\Delta G_{CO_2 \text{ cap.}}$ (kcal/mol)	$\Delta G_{\text{decomp.}}$ (kcal/mol)	$\frac{\Delta G_{CO_2 \text{ cap.}}}{\Delta G_{\text{decomp.}}}$	
Ti	-69.9	-39.2	1.78	> 1
Zr	-54.3	-10.9	4.98	
Hf	-53.6	-12.9	4.16	
V	-73.2	-82.3	0.89	~ 1
Nb	-58.6	-55.2	1.06	
Ta	-56.2	-53.7	1.05	
Cr	-62.8	-114.4	0.55	< 1
Mo	-61.1	-104.0	0.59	
W	-59.0	-102.4	0.58	

Conclusion

$[Ti(O_2)_4]^{4-}$ is

1. Faster for DAC ✓
2. Stable ✓

Cost:

V_2O_5 \$300/mole

TiO_2 \$3/mole

M ΔG≠ (kcal/mol) =

IV	V	VI
Ti 18.6	**V** 22.3	**Cr** 31.2
Zr 22.8	**Nb** 26.5	**Mo** 33.1
Hf 22.7	**Ta** 26.7	**W** 34.2

Hirschi, J. S.; Nyman, M.; Zuehlsdorff, T. J. *Under Review JPC A.* **ChemRxiv**. DOI: 10.26434/chemrxiv-2024-blwjs

Conclusion

$[Ti(O_2)_4]^{4-}$ is

1. Faster for DAC ✓
2. Stable ✓

Cost:

V_2O_5 \$300/mole

TiO_2 \$3/mole

Promising

✗

M

$\Delta G^{\neq}$

(kcal/mol)

=

III	IV	V	VI	VII
Sc ?	**Ti** 18.6	**V** 22.3	**Cr** 31.2	**Mn** ?
Y ?	**Zr** 22.8	**Nb** 26.5	**Mo** 33.1	**Tc** ?
	Hf 22.7	**Ta** 26.7	**W** 34.2	**Re** ?

<u>Hirschi, J. S.</u>; Nyman, M.; Zuehlsdorff, T. J. *Under Review JPC A.* **ChemRxiv**. DOI: 10.26434/chemrxiv-2024-blwjs

Acknowledgments

Zuehlsdorff Group

Nyman Group

MaD Lab

DOE Grant DE-SC0022278

Chemistry Department Summer Fellowship (2021)

Publications

1. **Hirschi, J. S.**; Nyman, M.; Zuehlsdorff, T. J. Electronic Structure and CO_2 Reactivity of Group IV/V/VI Tetraperoxometalates. *Under Review*. *ChemRxiv.*
2. Ribó, E. G.; Mao, Z.; **Hirschi, J. S.**; Linsday, T.; Bach, K.; Walter, E. D.; Simons, C. R.; Zuehlsdorff, T. J.; Nyman, M. Implementing vanadium peroxides as Direct Air Carbon Capture Materials. *Chem. Sci.* 2024, *15*, 1700-1713.

Appendix Slides

Functional Bechmarking

Table S3: Gibbs activation barrier of the rate-determining step, int2 $\longrightarrow$ ts2, with various DFT functionals. Values are in units of kcal/mol.

M	PBE	PBE0	M06-2X	MN15	CAM-B3LYP	CAM-B3LYP-D3
Ti	2.9	15.3	25.9	20.1	18.6	18.6
Zr	6.9	19.4	30.3	24.3	22.8	22.7
Hf	6.5	19.3	29.7	23.6	22.7	22.8
V	3.3	17.9	31.2	24.1	22.3	22.4
Nb	6.9	22.7	33.8	27.5	26.5	26.5
Ta	8.2	23.0	33.8	27.6	26.7	26.8
Cr	10.2	27.0	40.3	32.8	31.2	30.9
Mo	8.9	28.5	40.5	34.6	33.1	33.1
W	12.4	30.4	40.8	35.6	34.2	34.2

Peroxide Orbitals

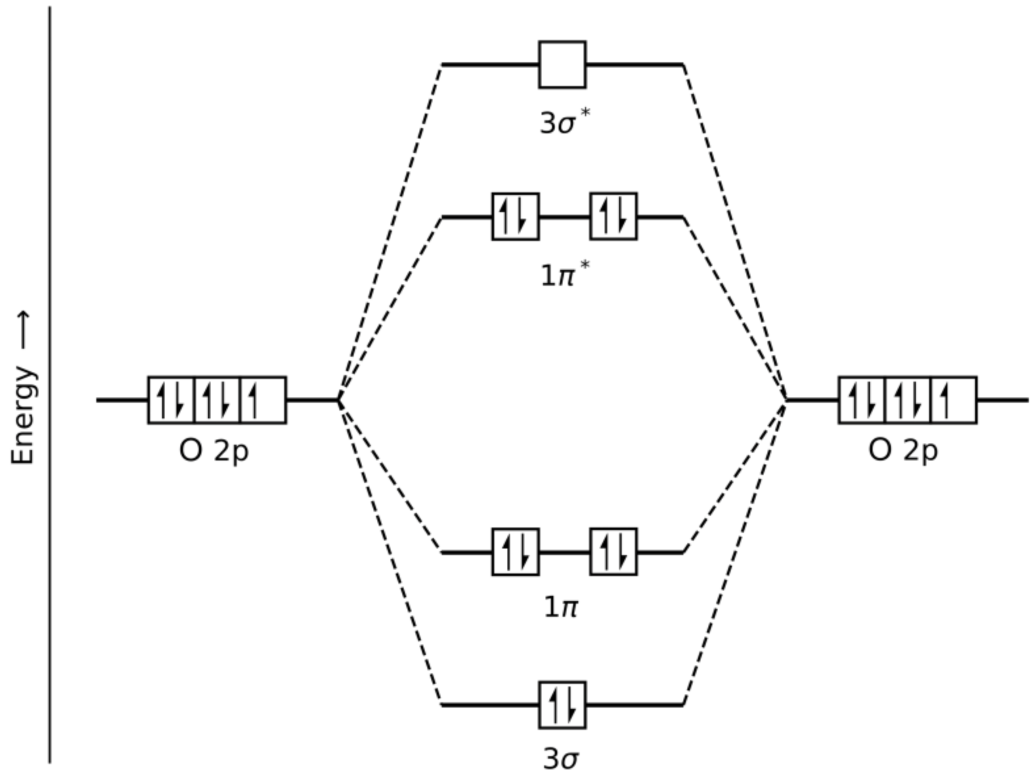
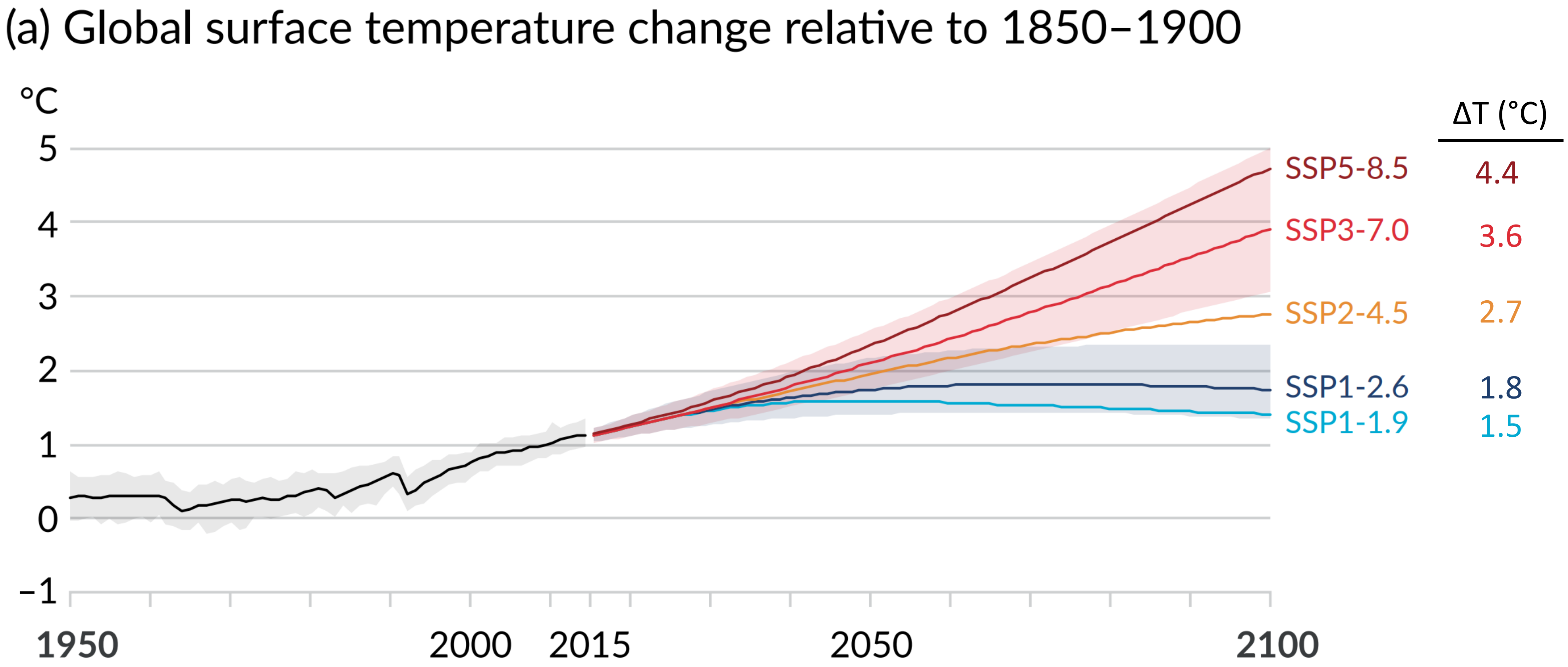


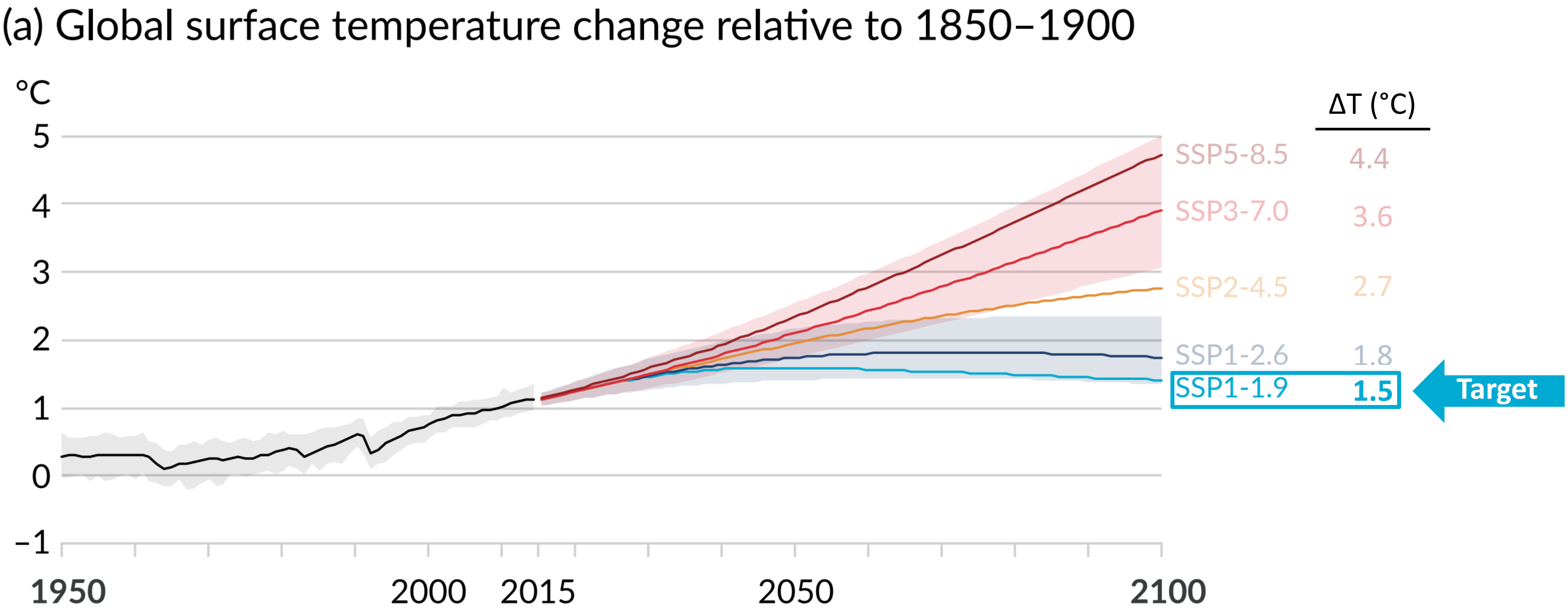
Figure S5: Qualitative molecular orbital diagram of the peroxide dianion, O_2^{2-}, showing two sets of occupied π and π^* orbitals.

Climate Outcomes



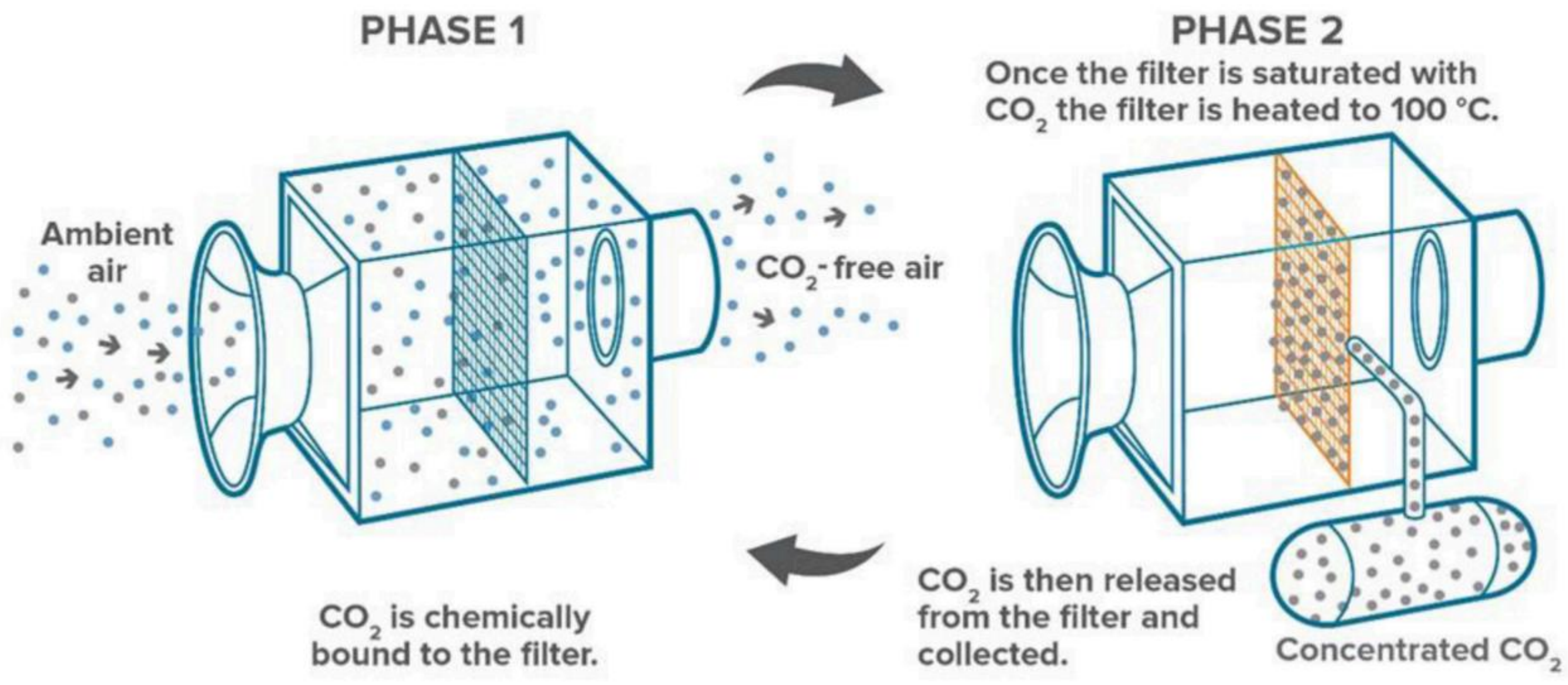
Masson-Delmotte, V.P.; et al. IPCC, 2021: Summary for Policymakers.

Climate Outcomes



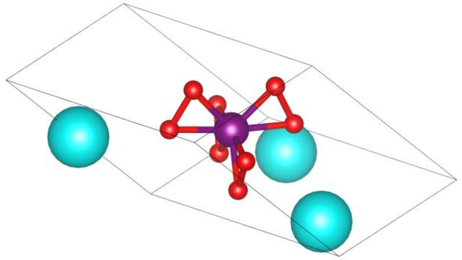
Masson-Delmotte, V.P.; et al. IPCC, 2021: Summary for Policymakers.

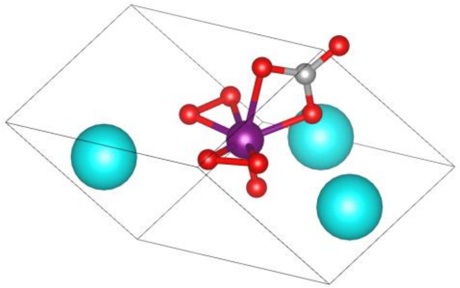
Direct Air Capture (DAC)

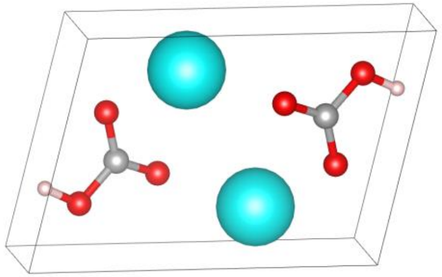


Beuttler, C.; et al. *Front. Clim.* **2019**, *1*, 10.

Solid-state Thermodynamics





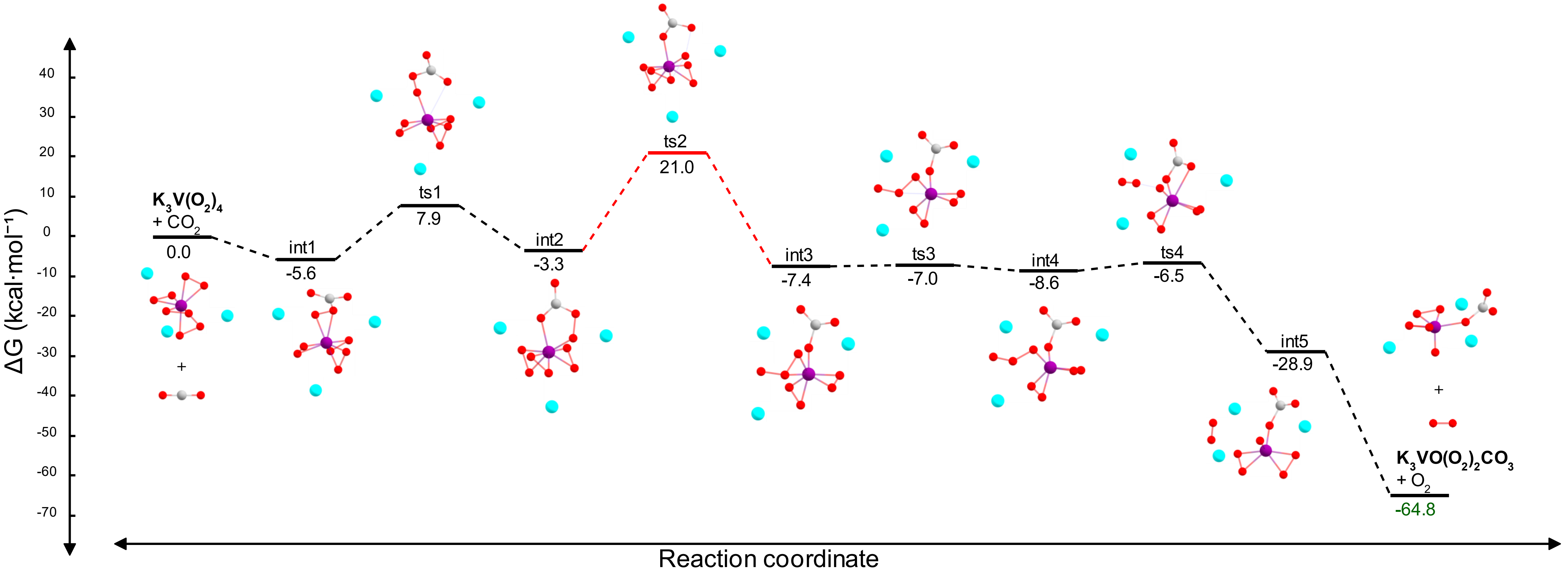


carbon capture

decomp.

Reaction	$\Delta G_{298\,K}$ (kcal/mol)
$K_3V(O_2)_4 + CO_2 \rightarrow K_3VO(O_2)_2CO_3 + O_2$	-52.1
$K_3V(O_2)_4 + 2CO_2 + H_2O \rightarrow KVO_3 + 2KHCO_3 + O_2$	-92.8
$K_3V(O_2)_4 + H_2O \rightarrow KVO_3 + 2KOH + 2O_2$	-58.2
$K_3VO(O_2)_2CO_3 \rightarrow K_3VO_4 + CO_2 + O_2$	-14.5

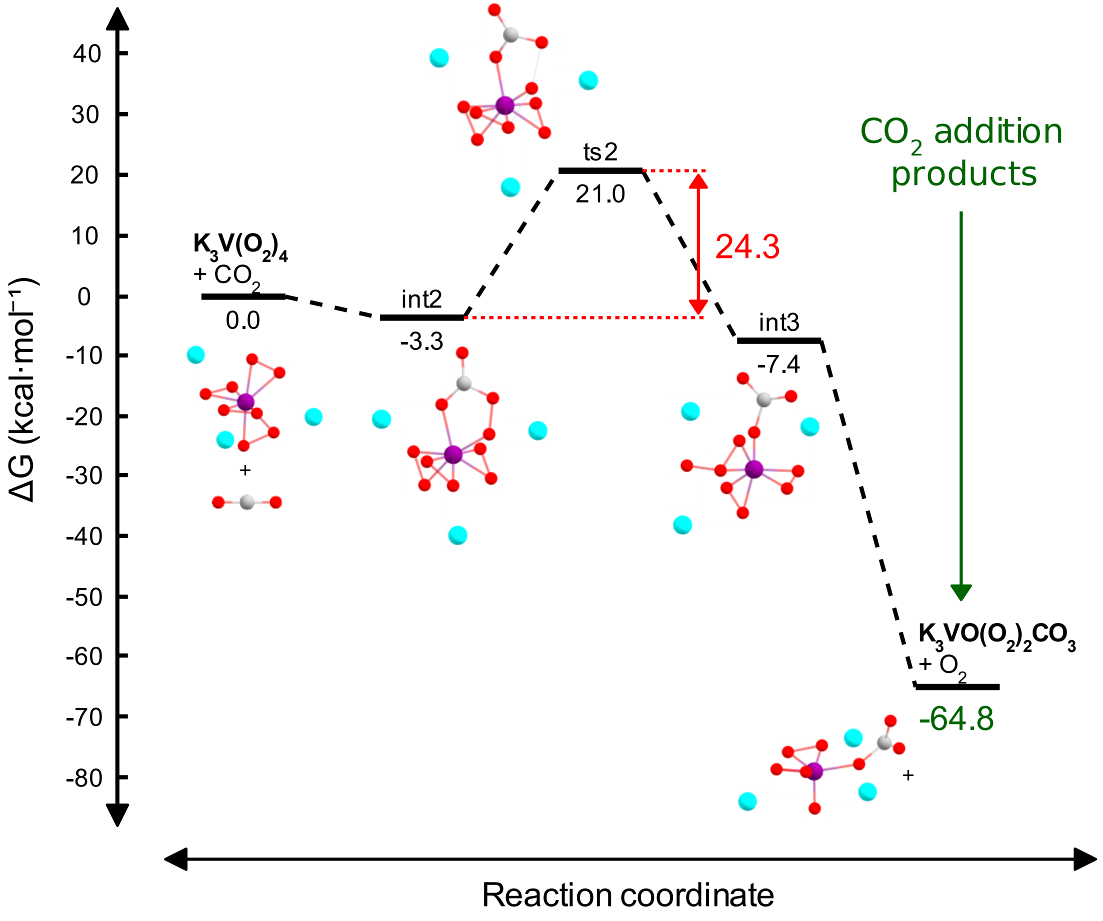
$K_3V(O_2)_4 + CO_2$ Mechanism



Simplified Mechanism

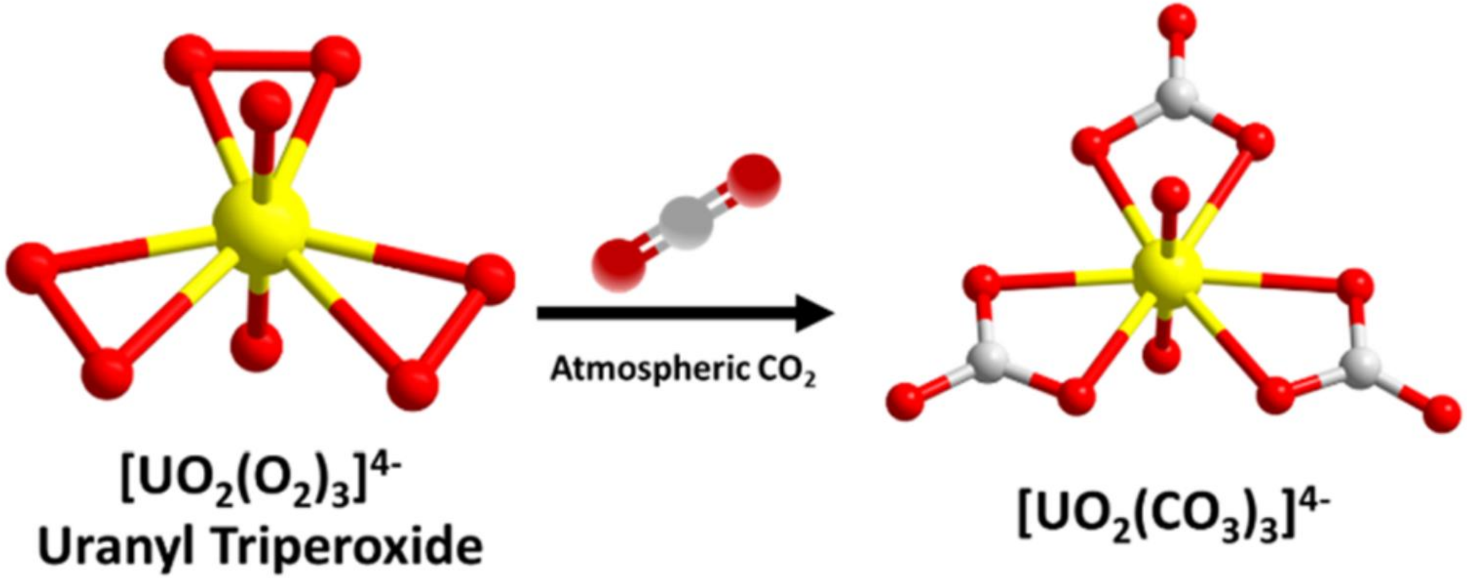
$CO_2 \rightarrow CO_4^{2-} \rightarrow CO_3^{2-}$

$$\Delta G^{\neq}_{\mathrm{RD}} = 24.3 \text{ kcal/mol}$$
$$\Delta G_{\mathrm{rxn}} = -64.8 \text{ kcal/mol}$$



DAC with Uranium?

Prof. May Nyman



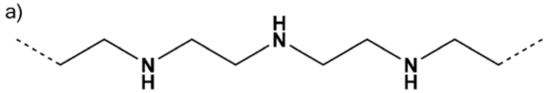
DAC Commercialization

Alkali hydroxides

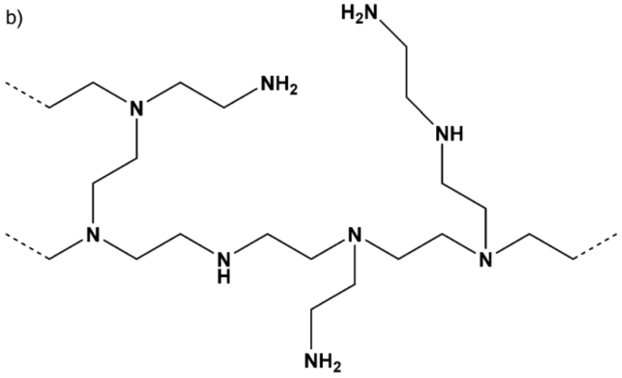
$$2NaOH\ (aq) + CO_2\ (g) \rightarrow Na_2CO_3\ (aq) + H_2O\ (l)$$

Amine-functionalized solids

a)



b)



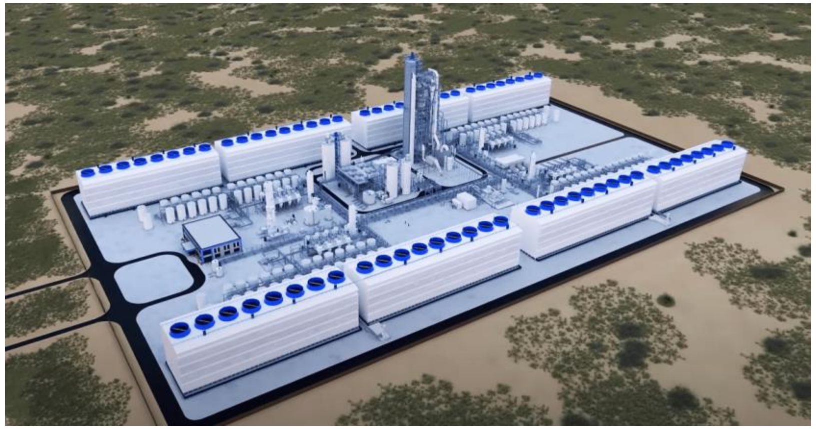
Stolaroff, J. K.; et al. *Environ. Sci. Tech.* **2008,** *42* (8), 2728.

Shi, X.; et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 6984.

DAC Commercialization

Carbon Engineering

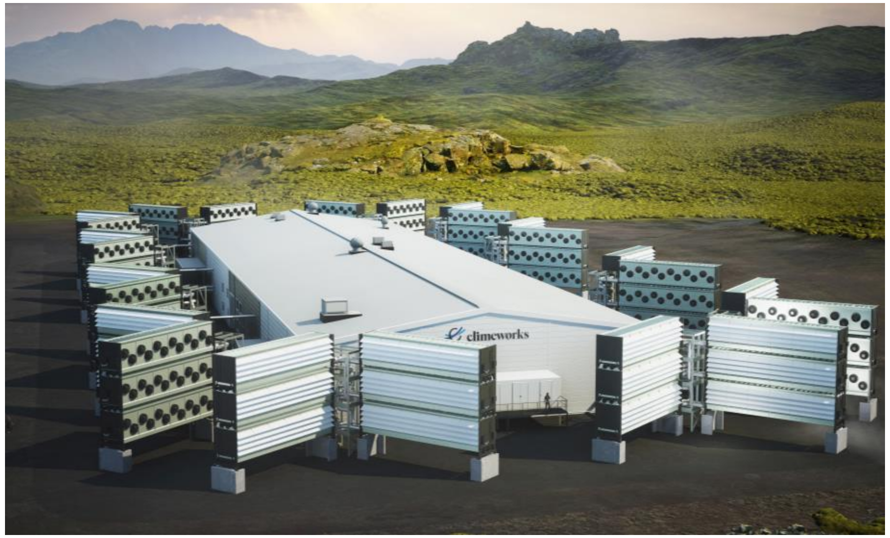
Stratos, Late 2024 (planned)



500,000 t-CO_2/yr

climeworks

Mammoth, May 2024



36,000 t-CO_2/yr

https://www.bloomberg.com/news/articles/2023-11-07/blackrock-bets-550-million-on-occidental-carbon-capture-plant

https://www.reuters.com/business/environment/climeworks-opens-worlds-largest-plant-extract-co2-air-iceland-2024-05-08/

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