

Sulphur dioxide oxidation mechanism on Pt surfaces: A DFT study

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SOLEMN DECLARATION

I, Theunis Nel, student number 21715440, declare herewith that the dissertation entitled Sulphur dioxide oxidation mechanism on Pt surface: A DFT study, which I herewith submit to the North-West University is in compliance/partial compliance with the requirements set for the degree: Master of Science in Chemistry is my own work, has been text-edited in accordance with the requirements and has not already been submitted to any other university.

PREFACE AND ACKNOWLEDGEMENTS

In this thesis, the properties of sulphur dioxide (SO_2) adsorption, the adsorption of other sulphur oxides, the co-adsorption properties of SO_2 and H_2O , and the co-adsorption of H_2SO_4 and H_2 on Pt(111), are discussed. Both the energy and the charge properties of adsorbed species involved in the Hybrid sulphur cycle, are discussed.

This thesis is written in a style which complies to General Academic Rules for Masters Studies at the North-West University, South Africa. This thesis is presented in chapter format and consists of five chapters and an appendix. Additional supplementary material, containing the atom coordinates of optimised structures, is provided in a separate document, and may be found at VAN SITTEERT, CORNIE; NEL, THEUNIS (2020): Sulphur dioxide oxidation mechanism on Pt surfaces: A DFT study. North-West University. Dataset. https://dayta.nwu.ac.za/articles/dataset/Sulphur_dioxide_oxidation_mechanism_on_Pt_surfaces_A_DFT_study/13283984 [1].

Although some journeys for the acquirement of knowledge are perused alone, contributions from others towards its successful completion is impossible without the aid of others. Often, the journeys wherein knowledge is pursued together, are accompanied by a higher probability of success than those attempted alone. I have been fortunate enough not to have walked this journey alone. I would like to thank, among others, my study leaders, Prof C.G.C.E. van Sittert and Dr M.J. Ungerer, for their mentorship, patience and guidance towards the completion of this dissertation.

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged. Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the NRF.

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CONFERENCE CONTRIBUTIONS

Oral presentation at the student symposium of the “Suid-Afrikaanse Akademie vir Wetenskap en Kuns” on 1 November 2019 at the university of the Free-State, South Africa titled “SO₂-oksidasiemeganisme op ‘n Pt-oppervlak: ‘n Digtheidsfunksionaalondersoek”.

Oral presentation at the Centre for High Performance Computing 2020 National Conference 30 November 2020 – 2 December 2020.

ABSTRACT

Lately, significant interest has risen towards the development of renewable energy in order to lower fossil fuel consumption and its environmental impact. Hydrogen (H_2) has been proposed as a viable alternative to fossil fuels due to its high energy per unit mass, as well as its low environmental impact. Despite numerous methods that exist for obtaining H_2 , production of H_2 is often difficult. Among various viable processes utilised to produce H_2 , is the Hybrid Sulphur (HyS) cycle wherein sulphur dioxide (SO_2) and water (H_2O) is thermo-electrochemically converted into sulphuric acid (H_2SO_4) and H_2 . Platinum (Pt) has proven to be an efficient catalyst for the HyS cycle, producing a high purity of H_2 . However, uncertainties regarding SO_2 - H_2O interaction on the Pt surface persist, complicating efforts towards the development of catalyst with high efficiency.

Although various experimental investigations have been performed, no absolute conclusions regarding the HyS cycle mechanism have thus far been made. Since little is still understood regarding the fundamental description of the HyS cycle, and in particular, the interaction between SO_2 and H_2O on the Pt surface, this dissertation fundamentally investigates the energetic and electronic properties of co-adsorbed SO_2 and H_2O on a Pt surface. Through density functional theory (DFT) analysis, it is observed that the adsorption of H_2O on the Pt surface is significantly influenced by the presence of pre-adsorbed SO_2 , both in terms of adsorption energy and adsorption geometry. In addition, when comparing the influence of pre-adsorbed SO_2 and pre-adsorbed H_2O on the H_2O adsorption process, it is observed that H_2O adsorption is influenced more by pre-adsorbed SO_2 than by pre-adsorbed H_2O .

Furthermore, the adsorption of other sulphur containing species such as sulphur monoxide SO and sulphuric acid H_2SO_4 (both cis- and trans-isomers), as well as the adsorption of H_2 on Pt(111) are discussed. The co-adsorption of H_2SO_4 and H_2 on Pt(111) is also discussed and compared to the co-adsorption of SO_2 and H_2O .

Finally, possible SO_2 oxidation mechanisms for the HyS reaction on Pt(111) were investigated. Both the Eley-Rideal and Langmuir-Hinshelwood mechanisms were evaluated on pristine Pt(111) with the former mechanism identified as occurring by preference.

Key words: Hybrid sulphur cycle; Platinum; Sulphur dioxide, Adsorption; Co-adsorption; Oxidation mechanism

OPSOMMING

'n Beduidende belangstelling in die ontwikkeling van hernubare energie, ten einde fossielbrandstofverbruik as ook die omgewingsimpak daarvan te verlaag, het in die nabye verlede ontstaan. Waterstof (H_2) is, as gevolg van die hoë energie per eenheidsmassa as ook lae omgewingsimpak daarvan, as 'n moontlike vatbare alternatief tot fossielbrandstowwe, voorgestel. Alhoewel verskeie metodes vir die verkryging van H_2 bestaan, is die vervaardiging van H_2 dikwels moeilik. Onder die verskeie moontlike prosesse wat vir die vervaardiging van H_2 aangewend word is die hibried-swawel(HyS)-siklus, waar swaweldioksied (SO_2) en water (H_2O) termochemies na swawelsuur (H_2SO_4) en H_2 omgeskakel word. Daar is bewys dat Platinum (Pt), wat 'n hoë suiwerheidsgraad H_2 te lewer, as 'n doeltreffende katalisator vir die HyS-siklus kan dien. Nietemin, bestaan daar steeds onsekerheid betreffende die SO_2 - H_2O -interaksie op die Pt-oppervlak, wat die poging om meer effektiewe katalisatore te ontwikkel, bemoeilik.

Alhoewel verskeie eksperimentele ondersoeke reeds voltooi is, kon geen onvoorwaardelike gevolgtrekkings rondom die HyS-siklusmeganisme sover bereik word nie. Aangesien daar steeds min rakende die fundamentele beskrywing van die HyS-siklus verstaan word, en in die besonder, die interaksie tussen SO_2 en H_2O op die Pt-oppervlak, ondersoek hierdie verhandeling fundamenteel die energetiese en elektroniese eienskappe van gesamentlik-geadsorbeerde SO_2 en H_2O , op die Pt-oppervlak. Deur middel van digtheidsfunksionaalteorie-analise (DFT), is daar waargeneem dat H_2O -adsorpsie op die Pt-oppervlak, beduidend deur die teenwoordigheid van voor-af geadsorbeerde SO_2 , beide met betrekking tot adsorpsie-energie en adsorpsie-geometrie, beïnvloed word. Daar is ook waargeneem dat as die invloed van voor-af geadsorbeerde SO_2 en voor-af geadsorbeerde H_2O op die H_2O -adsorpsieproses vergelyk word, die H_2O -adsorpsie meer deur voor-af geadsorbeerde SO_2 as deur voor-af geadsorbeerde H_2O beïnvloed word.

Verder, is die adsorpsie van ander swawelbevattende spesies soos swawelmonoksied SO en swawelsuur H_2SO_4 (beide cis- en trans-isomere), as ook die adsorpsie van H_2 op Pt(111), bespreek. Die gesamentlike adsorpsie van H_2SO_4 en H_2 op Pt(111) is ook bespreek en met die gesamentlike adsorpsie van SO_2 en H_2O vergelyk.

Laastens, is moontlike SO_2 -oksidasiemeganismes vir die HyS-reaksie op Pt(111) ondersoek. Beide die Eley-Rideal- en Langmuir-Hinshelwoodmeganismes op suiwer Pt(111) is bestudeer, waartydens die eersgenoemde meganisme geïdentifiseer is as die meganisme wat by voorkeur plaasvind.

Sleutelwoorde: Hibried-swawel-siklus; Platinum; Swaweldioksied, Adsorpsie;Gesamentlike adsorpsie; Oksidasiemeganisme

TABLE OF CONTENTS

SOLEMN DECLARATION	I
PREFACE AND ACKNOWLEDGEMENTS	II
LIST OF PUBLICATIONS.....	III
CONFERENCE CONTRIBUTIONS	IV
ABSTRACT.....	V
LIST OF ABBREVIATIONS AND SYMBOLS	XII
CHAPTER 1 INTRODUCTION	1
1.1 Background to study	1
1.2 Problem Statement	3
1.3 Aim and Objectives	3
1.4 Layout of dissertation.....	4
CHAPTER 2 LITERATURE STUDY	6
2.1 Introduction	6
2.2 Adsorption of other sulphur oxides	9
2.3 Co-adsorption of SO ₂ with H ₂ O and O ₂	9
2.4 Adsorption and surface-coverage effects	10
2.5 Adsorption modes and favoured adsorption sites of sulphur oxides	11
2.6 Factors influencing SO ₂ adsorption on Pt surfaces	15
2.6.1 The influence of temperature	15
2.6.2 Neutral and ionic sulphur oxides	17

2.7	Structural properties of adsorbed sulphur oxides	17
2.8	Electronic properties of adsorbed sulphur oxides	19
2.9	Adsorption on Pt alloys.....	21
2.10	The influence of SO₂ adsorption on the electronic properties of metals	21
2.11	Adsorption and molecular orbitals.....	23
2.12	Describing electrons.....	24
2.13	An overview of molecular modelling theory and DFT	24
2.13.1	DFT approximations.....	25
2.13.2	DFT and solid-state systems.....	26
2.13.3	Hybrid functionals and DFT.....	29
2.13.4	The Perdew-Burke-Erznherhof functional	29
2.14	Molecular Modelling of adsorption on a metal surface	30
2.15	Describing electronic behaviour of adsorption systems	31
2.16	Conclusion.....	32
CHAPTER 3	COMPUTATIONAL METHODS	33
3.1	Introduction	33
3.2	Modelling of Pt bulk and the pristine Pt(111) surface	34
3.2.1	Calculation Model.....	34
3.2.2	Vienna Ab-Initio Simulation Package (VASP 5.4.1)	35
3.2.2.1	The INCAR-File.....	36
3.3	Lattice Parameter	39
3.4	Creating the Pt(111) and Pt Surface Stability	39

3.5	Modelling of gas molecules	41
3.5.1	Calculation Model.....	41
3.5.2	Gas Molecules	41
3.6	Adsorption, Sequential Co-adsorption and Oxidation of SO₂ on Pt(111)	42
3.6.1	Surface Adsorption, Relaxation and energy determination of adsorbed systems	42
3.6.2	Sequential co-adsorption of SO ₂ and H ₂ O	44
3.6.3	SO ₂ Oxidation with H ₂ O	44
3.7	Bader Charge Analysis	45
3.8	Conclusion.....	46
CHAPTER 4	RESULTS AND DISCUSSION	48
4.1	Introduction	48
4.2	Modelling of pristine Pt bulk and Pt(111) systems	49
4.2.1	Pristine Pt bulk	50
4.2.2	Determination of vacuum spacing and energy of Pt(111) system.....	51
4.2.3	Structural properties of pristine Pt(111)	53
4.2.4	Bader Analysis for Pt(111) system	54
4.3	Modelling of isolated adsorbates	55
4.3.1	Isolated gas species (adsorbates)	56
4.3.2	SO ₂ oxidation reaction energies in the gas phase	60
4.4	SO₂ adsorption on Pt(111).....	61
4.4.1	Adsorption energy and properties of SO ₂	62
4.4.2	Bader Analysis of PtSO _{2(ad)}	66

4.5	Adsorption of other SO_x species on Pt(111).....	68
4.5.1	Adsorption energies and geometries of SO _x (x=1,3).....	68
4.5.2	Bader analysis of adsorbed oxidised SO _x adsorption systems	73
4.6	Adsorption of H₂SO_y species (y = 3, 4) on Pt(111)	74
4.6.1	Adsorption energy of H ₂ SO ₄	74
4.6.2	Adsorption energy of H ₂ SO ₃	78
4.7	Bader analysis of adsorbed oxidised PtH_nSO_{x(ad)} systems	79
4.7.1	PtH ₂ SO _{4(ad)} Bader Analysis	79
4.7.2	PtH ₂ SO _{3(ad)} Bader Analysis	80
4.8	Adsorption of ionic H_nSO₄^{x-} species on Pt(111) (n = 1; x = 1)	81
4.8.1	Adsorption of HSO ₄ ⁻	81
4.9	Adsorption of molecules that may be co-adsorbed with SO₂ on Pt(111)	83
4.9.1	Adsorption energies of molecules that may co-adsorb with SO ₂	83
4.9.2	Bader Analysis of molecules that may co-adsorb with SO ₂	86
4.10	Adsorption energies of multiple co-adsorbed molecules on Pt(111)	87
4.10.1	Adsorption energies of 2SO ₂ co-adsorption arrangements	87
4.10.2	Adsorption energies of SO ₂ + H ₂ O co-adsorption arrangements	91
4.10.3	Adsorption energies of SO ₂ + 2H ₂ O co-adsorption arrangements	95
4.10.4	Adsorption energies of 2SO ₂ + H ₂ O co-adsorption arrangements	100
4.10.5	Adsorption energies of H ₂ SO ₄ + H ₂ co-adsorption arrangements	104
4.10.6	Bader Analysis of the SO ₂ + H ₂ O co-adsorbed system.....	107
4.10.7	Bader Analysis of co-adsorbed SO ₂ + 2H ₂ O on Pt(111)	108
4.11	SO₂ oxidation on Pt(111)	109

4.11.1	Oxidation energy of adsorbed SO ₂ on Pt(111).....	109
4.11.2	The SO ₂ oxidation mechanism on Pt(111).....	110
4.12	Conclusion.....	114
CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS		116
5.1	Conclusions.....	116
5.2	Recommendations regarding Future Research	117
REFERENCES.....		120
CHAPTER 6 APPENDIX.....		134
6.1	Pt(111) POSCAR file.....	134
6.2	Stackgen and Metadise	135
6.3	POSCAR and CONTCAR files	138
6.3.1	Optimisation POSCAR input file.....	139
6.3.2	Optimisation CONTCAR output file.....	140
6.4	Structure Optimisation (Relaxation) INCAR file	141
6.5	Single Point Energy determination INCAR file	143
6.6	Bader Analysis files	145

LIST OF ABBREVIATIONS AND SYMBOLS

Å	Ångström 1 Å = 10 ⁻¹⁰ m
ρ	Electron density
μ	Dipole-moment
ν	Frequency
μ _⊥	Perpendicular Dipole-moment
ψ	Wave function
$\vec{k}$	Wave vector
γ	Surface energy
AMO	Anti-bonding molecular orbital
BC	Bader Charge
BJ	Becke-Johnson
BMO	Bonding molecular orbital
CG	Conjugate gradient
CHPC	Centre for High Performance computing
DFT	Density Functional Theory
eV	Electron volt 1 eV ≡ 1.602 x 10 ⁻¹⁹ J
q _e ⁻	electron unit charge = 1.602 x 10 ⁻¹⁹ C
E _{free-ads}	Free-adsorption energy
E _{KE}	Kinetic energy
E _{ox}	Free-oxidation energy
E _{relaxed}	Free-energy of the relaxed surface wherein all atoms are allowed to move during an optimisation (relaxation) calculation
E _{unrelaxed}	Free-energy of the unrelaxed surface wherein all atoms are constrained to fixed positions and no atom movement is allowed
FCC	Face-centred-cubic
GGA	Generalised gradient approximation
HCP	Hexagonal close packing
HTF	Hartree-Fock
HK	Hohenberg-Kohn
HOMO	Highest occupied molecular orbital
HOR	Hydrogen oxidation reaction
HyS	Hybrid Sulphur cycle
KS	Kohn-Sham

L	Ligand
LDA	Local density approximation
LMTOs	Linearized muffin tin orbitals
LP	Lattice parameter
LUMO	Lowest unoccupied molecular orbital
M	Metal
MM	Molecular Mechanics
O _{pad}	Pre-adsorbed oxygen
ORR	Oxygen reduction reaction
PAW	Projector augmented wave
PBE	Perdew-Burke-Erznerhoff
Pt(111)	Pt 111 Miller surface
PW91	Perdew-Wang 91
SDE	SO ₂ depolarised electrolyser
T	Temperature
TPD	Temperature Programmed Desorption
V _{ad}	Metal-adsorbate matrix element
VASP	Vienna Ab-Initio Simulation Package
X _a	Atop-positioned atom
X _b	Bridging atom
X _f	FCC-positioned atom
X _h	HCP-positioned atom
X,Y	Distinguishable gas molecules or ions

LIST OF TABLES

Table 2.1:	Structural properties of the most stable adsorption geometries of some adsorbed sulphur oxides, reported in literature	17
Table 4.1:	Energies of different unit cell lattice parameter (LP) values for a primitive cell containing a single Pt atom	50
Table 4.2:	Energies for the pristine Pt(111) system with different vacuum spacings perpendicular to the surface	52
Table 4.3:	Cartesian coordinates and Bader charges of Pt atoms in pristine Pt(111) consisting of 64 atoms.....	54
Table 4.4a:	Calculated bond lengths (in Å) of isolated gaseous sulphur oxides (Literature values in parenthesis [135,152–154])	57
Table 4.5:	Calculated bond angles (in degrees °) of isolated (non-linear) gas species (Literature values in parenthesis [135,152,153,155])	58
Table 4.6:	Energies of optimised isolated gas species.....	59
Table 4.7:	Gas-phase oxidation energies.....	60
Table 4.8:	Adsorption energies of some SO ₂ adsorption geometries	63
Table 4.9:	Comparison of the structural properties of isolated and adsorbed SO ₂ and three directly bonded Pt atoms.....	66
Table 4.10:	Bader Charge properties of atoms in the isolated molecule in comparison to the adsorption system in Figure 4.9.....	67
Table 4.11:	Adsorption energies and distances of different SO adsorption geometries on Pt(111).....	69
Table 4.12:	Structural properties of FCC-η ¹ -S _f adsorbed SO	70
Table 4.13:	Adsorption energies of various SO ₃ ²⁻ adsorption geometries	72
Table 4.14:	Adsorbed SO _x Bader properties	73

Table 4.15:	Adsorption free-energies of various cis- and trans-H ₂ SO _{4(ad)} adsorption geometries.....	76
Table 4.16:	Structural properties of isolated and adsorbed cis- and trans-H ₂ SO ₄	78
Table 4.17:	Bader Differences in atoms as a result of the adsorption of cis-H ₂ SO ₄ in the FCC- η^2 -H _a ,H _a -S _b geometry	80
Table 4.18:	Bader Differences in atoms as a result of the adsorption of trans-H ₂ SO ₄ in the HCP- η^3 -H _a ,O _a ,O _a -S _h geometry	80
Table 4.19:	Bader Charges of H ₂ SO ₃ in the gas and FCC- η^3 -H _a ,O _a ,O _a adsorbed system	81
Table 4.20:	Adsorption free-energies of various HSO ₄ ⁻ adsorption geometries on Pt(111).....	82
Table 4.21:	Adsorption Free-Energies and structural properties of various species that may be co-adsorbed with SO ₂ on Pt(111), i.e. X _(g) → X _(ad)	84
Table 4.22:	Structural properties of isolated and η^1 -O _a adsorbed H ₂ O	85
Table 4.23:	Bader charge of co-adsorbable species on Pt(111)	86
Table 4.24:	Total Adsorption free-energies of two co-adsorbed SO ₂ molecules on Pt(111) i.e., 2SO _{2(g)} → 2SO _{2(ad)}	89
Table 4.25:	Adsorption energies of SO _{2(ad)} + H ₂ O _(ad) co-adsorption arrangements	92
Table 4.26:	Adsorption energies of the SO _{2(ad)} + H ₂ O _(ad) + H ₂ O _(g) → SO _{2(ad)} + 2H ₂ O _(ad) reaction step leading to the arrangements in Figure 4.23	97
Table 4.27:	Adsorption energies of co-adsorbed 2SO _{2(ad)} + H ₂ O _(ad) arrangements i.e. 2SO _{2(g)} + H ₂ O _(g) → 2SO _{2(ad)} + H ₂ O _(ad)	101
Table 4.28:	Adsorption energies of the 2SO _{2(ad)} + H ₂ O _(g) → 2SO _{2(ad)} + H ₂ O _(ad) step	102
Table 4.29:	Adsorption energies of cis-H ₂ SO ₄ + H ₂ co-adsorption arrangements on Pt(111).....	106
Table 4.30:	Bader Charges and Bader Charge differences of atoms in the SO _{2(ad)} + H ₂ O _(ad) co-adsorption system	107

Table 4.31:	Bader Charge analysis of the $\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}$ co-adsorption system.....	109
Table 4.32:	Adsorption energies of the most stable adsorption geometries of various molecules on pristine Pt(111)	110
Table 4.33:	Energies of the most stable co-adsorption arrangements on pristine Pt(111).....	110

LIST OF FIGURES

Figure 1.1:	The HyS cycle employed for the production of H ₂	2
Figure 1.2:	Layout of this dissertation	4
Figure 2.1:	(a) O _a and (b) S _a adsorbed SO ₂ on Pt(111).....	11
Figure 2.2:	Examples of perpendicular (a) and parallel (b) adsorbed SO ₂ on Pt(111)	12
Figure 2.3:	Different possible adsorption sites on Pt(111) namely FCC (green circle); atop (red circle); HCP (teal circle) and bridge (yellow circle).....	12
Figure 2.4:	Some SO ₂ adsorption geometries (a) η^2 -FCC-S _b O _a ; (b) HCP- η^3 -S _a O _a O _h and (c) FCC- η^1 -O _a S _f possibilities on Pt(111) with the adsorption site of each atom marked with subscripts	13
Figure 3.1:	Flow diagram of the methodology followed in this study	34
Figure 3.2:	(a) Adsorption sites on Pt(111) (FCC=green; atop=red; HCP=cyan; bridge=yellow); (b) Parallel lying H ₂ O; (c) Perpendicular standing H ₂ O	42
Figure 4.1:	Outline of Chapter 4	49
Figure 4.2:	Energy profile of different lattice parameters for the determination of optimal cell dimensions.	51
Figure 4.3:	(a) Relaxed Pt(111) system energy and (b) Energy difference between relaxed and unrelaxed systems as a function of vacuum spacing.	52
Figure 4.4:	Top (left) and side (right) view of pristine Pt(111).....	53
Figure 4.5:	Molecular structures of gas species, SO ₂ , SO, SO ⁺ , SO ₃ , SO ₃ ²⁻ , cis-H ₂ SO ₄ , trans-H ₂ SO ₄ , SO ₄ ²⁻ , HSO ₄ ⁻ , trans-H ₂ SO ₃ , H ₂ , H ₂ O, H ₃ O ⁺ and O ₂ . Standard colours are used throughout for hydrogen, oxygen and sulphur as white, red and yellow, respectively.	56
Figure 4.6:	Top and side views of different SO ₂ adsorption geometries on Pt(111)	62
Figure 4.7:	Adsorption energies of various SO ₂ geometries relative to the strongest adsorption geometry i.e. Figure 4.6a.....	64

Figure 4.8:	Top view of FCC-S _b O _a adsorbed SO ₂ on Pt(111).....	65
Figure 4.9:	Surfaces of charge density difference maxima (0.023474 e ⁻ ·Å ⁻³) in PtSO _{2(ad)} FCC-η ² -S _b O _a . (Positive, i.e. a loss of negatively charged electron density, and negative, i.e. a gain in negatively charged electron density, maxima are indicated by teal and yellow respectively.)	67
Figure 4.10:	Top and side views of various SO and SO ⁺ adsorption geometries on Pt(111).....	69
Figure 4.11:	Relative adsorption energies of different SO adsorption geometries on Pt(111).....	70
Figure 4.12:	Top and side views of various SO ₃ ²⁻ and SO ₃ adsorption geometries on Pt(111).....	71
Figure 4.13:	Relative adsorption energies of different SO ₃ ²⁻ adsorption geometries on Pt(111).....	72
Figure 4.14:	Top and side views of various cis- and trans-H ₂ SO _{4(ad)} adsorption geometries	75
Figure 4.15:	Relative adsorption energies of various cis- and trans-H ₂ SO ₄ adsorption geometries on Pt(111)	76
Figure 4.16:	Top and side view of the FCC-η ³ -H _a O _a O _a adsorption geometry of H ₂ SO ₃ on Pt(111)	78
Figure 4.17:	Adsorption geometries of HSO ₄ ⁻ on Pt(111).....	82
Figure 4.18:	Relative adsorption energies of various HSO ₄ ⁻ adsorption geometries on Pt(111).....	82
Figure 4.19:	Adsorption geometries of various co-adsorbed species on Pt(111)	84
Figure 4.20:	Adsorption free-energies of co-adsorbed species on Pt(111)	85
Figure 4.21:	Top and side views of various arrangements of two FCC-η ² -S _b O _a co-adsorbed SO ₂ molecules on Pt(111)	88
Figure 4.22:	Top and side views of SO _{2(ad)} + H ₂ O _(ad) co-adsorption arrangements on Pt(111).....	91

Figure 4.23:	$\text{SO}_2 + 2\text{H}_2\text{O}$ co-adsorption arrangements on Pt(111).....	96
Figure 4.24:	Energy diagram of sequential co-adsorption of one SO_2 with two H_2O on Pt(111) leading to $\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}$ adsorption arrangement 10 (Figure 4.23j)	99
Figure 4.25:	$2\text{SO}_2 + \text{H}_2\text{O}$ co-adsorption arrangements on Pt(111).....	101
Figure 4.26:	Sequential adsorption of two SO_2 with one H_2O on Pt(111).....	104
Figure 4.27:	cis- $\text{H}_2\text{SO}_4 + \text{H}_2$ co-adsorption arrangements on Pt(111).....	105
Figure 4.28:	Atom positions in $\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}$ co-adsorption arrangement 10.....	108
Figure 4.29:	Energy-profile ^a of the Eley-Rideal (red) and Langmuir-Hinshelwood (blue) mechanisms for the HyS reaction $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2$ on pristine Pt(111); ^a Note that the energy is measured relative to the total energy of the reactants i.e. $\text{PtSO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$	112

CHAPTER 1 INTRODUCTION

1.1 Background to study

Due to the increasing demand for energy, the world's fossil fuel resources have come under increased strain [3]. In addition, the emission of pollutants from fossil fuel combustion have detrimental effects on the earth's environment [3,4]. Lead, mercury and other heavy metals, as well as greenhouse gasses, such as nitrogen oxides (NO_x), carbon dioxide (CO_2), sulphur dioxide (SO_2) and other sulphur oxides (SO_x), are among these pollutants that are emitted into the atmosphere [5,6]. The emission of sulphur dioxide (SO_2) by natural and anthropogenic sources leads to the formation of sulphuric acid (H_2SO_4), referred to as acid rain, in the earth's atmosphere by oxidation [3]. The proposed pathway of this reaction is the oxidation of SO_2 to form SO_3 , which then reacts with H_2O to form H_2SO_4 [3]. This H_2SO_4 has various detrimental effects on vegetation, agriculture and infrastructure [7]. The detrimental influence of H_2SO_4 on vegetation, and therefore important natural cycles such as the carbon and nitrogen cycles, further influences the concentration of greenhouse species in the atmosphere. Since greenhouse species, which often originate from the combustion of fossil fuels, contribute significantly towards global warming and climate change, alternative more environmentally friendly energy resources need to be identified and developed.

Some of these alternative more environmentally friendly energy resources are solar energy, wind, geothermal, wave and tidal energy sources, as well as the employment of hydrogen (H_2) as an energy carrier. Furthermore, H_2 may serve as a particularly viable option due to its high energy per unit mass, low impact on the environment as well as a significantly high efficiency, in comparison to other energy sources. Various methods are employed to obtain H_2 , among others, the electrolysis of H_2O , photo-catalytic H_2O splitting, photo-biological H_2O splitting as well as the ferrosilicon method [8–10]. Among the various technologies that are employed to obtain hydrogen is the hybrid sulphur (HyS) cycle. The HyS cycle is a thermo-electrical process wherein SO_2 and H_2O is converted into H_2SO_4 and H_2 . The H_2SO_4 is immediately recycled to the decomposition chamber. The most prominent advantages of the HyS cycle are the high purity of the obtained H_2 as well as that no other detrimental by-products are formed, making it a viable option for obtaining H_2 . However, some energy input is needed in the HyS cycle. The energy required in the HyS cycle, may be acquired through solar energy, instead of using fossil fuels as energy source, although development towards higher efficiencies in solar powered hydrogen production, is still required [11,12].

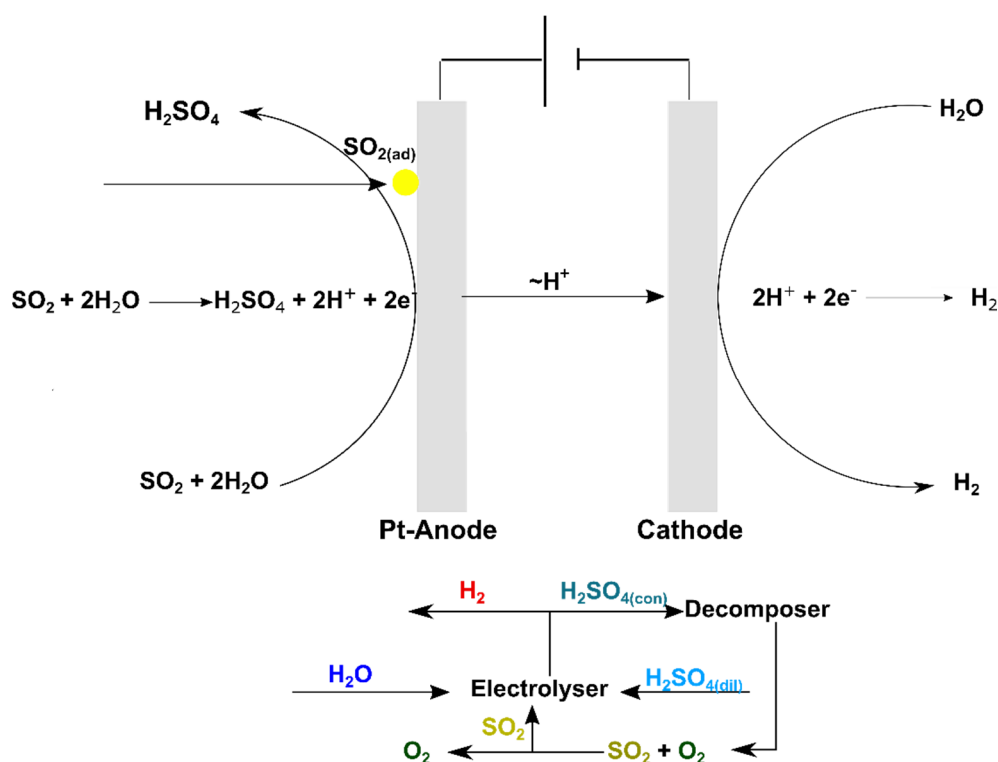
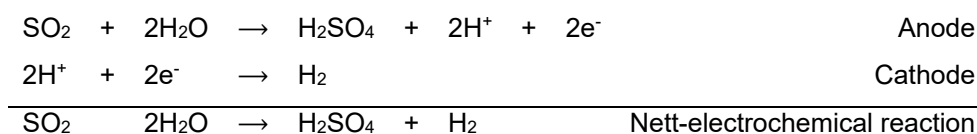


Figure 1.1: The HyS cycle employed for the production of H_2

The first step in the HyS cycle (Figure 1.1) is the thermal decomposition of H_2SO_4 to form SO_2 , H_2O and O_2 . The resulting SO_2 and H_2O react on the anode, in the SO_2 depolarised electrolyser (SDE), where it is subsequently electro-oxidised to form H^+ and H_2SO_4 [3]. The next step is the migration of H^+ through the electrolyser membrane to the cathode, where the H^+ is reduced to form $\text{H}_{2(\text{g})}$, while H_2SO_4 is simultaneously recirculated back to the decomposition chamber [3]. The net reaction is thus the splitting of H_2O into H_2 and O_2 . The overall half-reactions within the HyS cycle can be summarised as [3]:



In order for the efficient onset of the HyS cycle, a sufficient electro-catalyst, consisting of a suitable material, is required [13]. Both the anode and cathode are consequently required to consist of materials with sufficient reactivities, with a high selectivity towards the required reaction as well as being strongly corrosion-resistant. Currently, Pt serves as a popular catalyst in various processes, a particular example being the HyS cycle wherein Pt provides high reactivity towards catalysing SO_2 oxidation in the HyS cycle [13,14].

1.2 Problem Statement

Although Pt is currently mostly used as a catalyst in the HyS cycle, it is hampering the development of the HyS cycle for possible commercial application [13,14]. The reason being three-fold, namely, Pt is a rare and expensive resource, the stability of the Pt in H_2SO_4 is limited, and SO_2 poisoning occurs on Pt surfaces. To address these problems, more cost-effective, durable, and efficient catalysts are needed. However, before the replacement of Pt as the catalyst in the HyS cycle is considered, the mechanism of the oxidation of SO_2 with H_2O on a Pt surface, as well as the adsorption and oxidation of SO_2 on the Pt surface must be understood.

Although extensive research has been performed regarding SO_2 adsorption on Pt surfaces, little is known regarding the co-adsorption behaviour of SO_2 and H_2O on Pt(111). Additionally, the mechanistic description of the SO_2 reactions on the catalyst surfaces has not been studied in detail. One particular reaction, which is not well understood, is the oxidation of the adsorbed SO_2 with H_2O leading to the formation of H_2SO_4 on Pt(111).

In addition, since the adsorption and oxidation of SO_2 onto Pt catalysts pose a substantial problem towards catalyst efficiency and durability, further investigation regarding the behaviour of SO_2 on Pt surfaces is also necessary [15–19].

1.3 Aim and Objectives

In this dissertation the aim is to investigate SO_2 and H_2O co-adsorption as well as other sulphur oxide adsorptions on Pt(111), through the use of molecular modelling, in particular density functional theory, in order to aid in the development of an SO_2 oxidation mechanism.

The objectives included within this aim are the identification of the energetic, electronic and structural properties of the SO_2 adsorption, as well as its co-adsorption properties with H_2O on Pt(111). In particular, the sequential co-adsorption of SO_2 and H_2O , in terms of adsorption geometry, adsorption energy and Bader Charge properties between the adsorbates, is investigated.

Further objectives include investigating the adsorption properties of H_2SO_4 and other sulphur oxides on Pt(111), as well as determining how the adsorption properties of these additional sulphur species compare with that of SO_2 . Furthermore, since Pt(111) is a stepped surface it is in comparison to Pt(100) and Pt(001), characterised by a higher number of unique adsorption sites. Therefore, for a particular molecule, such as H_2O , a greater number of unique adsorption sites and consequently geometries are possible on Pt(111). Furthermore, a higher reactivity is

subsequently displayed by Pt(111) and thus, the Pt(111) surface is chosen as the specific surface for this investigation.

Bader charge analysis will be performed with the objective to identify possible charge transfer between the surface and the different adsorbates, as well as the possible charge transfer between co-adsorbed SO₂ and H₂O on the Pt surface.

Findings in this study will, furthermore, be compared to experimental observations and the feasibility of previously proposed mechanistic pathways will be investigated as well.

1.4 Layout of dissertation

In the following chapters of this dissertation, the literature on the adsorption properties of SO₂ is discussed, and specific limitations that exist are presented. A systematic description of the methodology taken in this dissertation is presented and discussed.

A schematic diagram of the layout of this thesis is illustrated in Figure 1.2

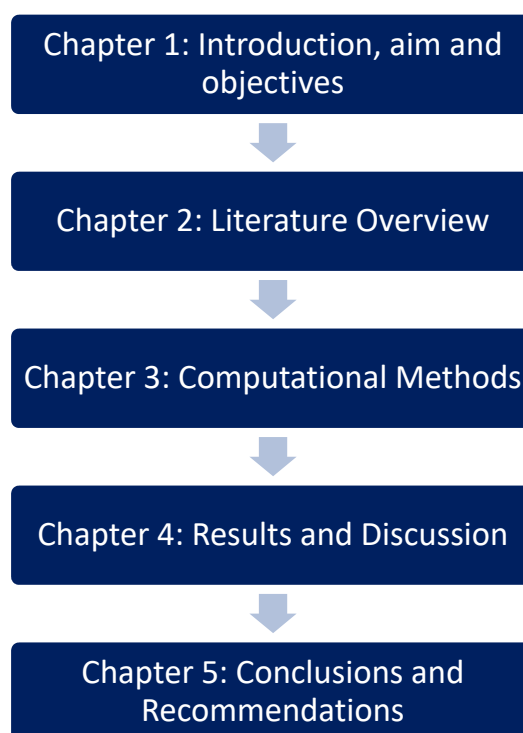


Figure 1.2: Layout of this dissertation

Chapter 2 consists of a literature overview of the HyS process and the adsorption of various sulphur oxides on Pt surfaces. The adsorption of these sulphur oxides at favoured adsorption sites, as stated in the literature, are reviewed. Both the structural and electronic properties of adsorbed sulphur oxides on Pt are presented. An overview of DFT in molecular modelling as well

as some DFT functionals of particular importance in crystalline solid-state systems are discussed briefly. Finally, some shortcomings that persist in the literature are identified, in particular concerning the co-adsorption of SO_2 and H_2O , as well as discrepancies over the oxidation mechanism of SO_2 on Pt. The discrepancies discussed in Chapter 2, in particular regarding the SO_2 adsorption and oxidation mechanism on Pt(111) are highlighted as a further requirement for a comprehensive investigation of the HyS cycle.

In Chapter 3, the method used in this study is discussed. The specific DFT model employed, namely the generalised gradient approximation (GGA) with the Perdew-Burke-Erznherhoff function is discussed. Additionally, the general parameters employed in each of the molecular systems as well as specific parameters unique to every molecular system are discussed. Following the detailed discussion on the methodology in this dissertation, results regarding the adsorption behaviour of SO_2 , other sulphur oxides and the co-adsorption of SO_2 with H_2O are discussed.

The adsorption analysis of various gas species on Pt(111) is evaluated in Chapter 4, both in terms of energy as well as charge-related properties. Specific similarities and differences between the adsorption behaviour of different molecular species relevant in the HyS cycle are presented and discussed. In addition, the relative adsorption strengths and geometries of various sulphur oxides and co-adsorbable species are compared as well. Furthermore, the influence of SO_2 on the adsorption of H_2O is discussed, both in terms of energy as well as in terms of electronic properties. Finally, the most favourable adsorption and co-adsorption arrangements of SO_2 and H_2O are identified.

In Chapter 5, final remarks on the specific influence of adsorbate-adsorbate interaction among co-adsorbed species are made, and the SO_2 oxidation mechanism on Pt(111) identified in Chapter 4 is discussed briefly. Recommendations towards further work investigating the oxidation mechanism of SO_2 on Pt surfaces, specifically in reference to the HyS cycle, are made.

Lastly, some examples of files required as input, as well as files that are obtained as output, in DFT molecular modelling with Vienna Ab-Initio Simulation Package are provided in the Appendix (Chapter 6). A complete collection of all the atom coordinate files used in this dissertation is provided in the Supplementary Material document (doi: 10.25388/nwu.13283984).

CHAPTER 2 LITERATURE STUDY

In this chapter, the use of metal catalysts, and in particular the use of platinum (Pt) in various applications are discussed. This study is concerned with the use of Pt as a heterogeneous catalyst, specifically for application as a catalyst in alternative energy processes such as the hybrid sulphur (HyS) to obtain H_2 . Consequently, properties regarding the interaction between Pt and adsorbing species, are discussed.

The working of the HyS cycle is discussed in detail including various difficulties associated with SO_2 in this process. In order to elaborate on the behaviour of SO_2 , the discussion will include not only the adsorption mechanisms of SO_2 on Pt, but also the co-adsorption with other species, in particular with H_2O . Factors that have been proposed to influence the behaviour of SO_2 on Pt are presented, and the structural and electronic properties of adsorbed sulphur oxides on Pt, are discussed. Adsorption on metal alloys is discussed briefly, and the electronic influence of adsorbed SO_2 on metal surfaces is debated. Furthermore, is a brief theoretical overview of the description of the electronic properties in heterogeneous catalysis, is discussed. Lastly, certain shortcomings in literature are summarised.

The study of reaction mechanisms, prediction of spectra and development of various scientific theories in the description of catalytic chemical reactions and its properties have received significant interest since the late 19th century. This interest has been a result of the development of molecular quantum theory, which aids in a better understanding of chemical processes and enhances the description of electron behaviour [20].

Furthermore, the utilisation of molecular modelling has significantly increased in popularity with respect to the studying of material properties and to aid in the identification of reaction mechanisms in particular for catalytic processes [21]. The selective study of specific undesirable reactions, such as corrosion and catalyst inhibition, have been enhanced through the utilisation of molecular modelling [22]. One particular advantage that molecular modelling provides is that the adsorption of specific species on surfaces can be studied without any interference by other compounds and that specific metal-adsorbate systems can be observed independently. Therefore the use of molecular modelling is briefly discussed here as well.

2.1 Introduction

The Hybrid Sulfur (HyS) cycle (as shown in Figure 1.1 p. 2) is among various sustainable technologies currently employed, to aid in reducing fossil fuel consumption [3,23–25]. The HyS cycle is a thermo-electrical process wherein sulphuric acid (H_2SO_4) is thermally decomposed at

$T > 1073.15 \text{ K}$ to form sulphur dioxide (SO_2), water (H_2O) and oxygen (O_2). Furthermore, the HyS cycle also employs platinum (Pt) as a catalyst for the reaction between SO_2 and H_2O to produce hydrogen (H_2) as energy carrier while recycling H_2SO_4 back to the decomposition chamber [3]. Some of the distinct advantages of the HyS cycle are among others, the high purity of the obtained H_2 , the simplicity of the cycle and the high energy density of H_2 [23]. The HyS cycle (Figure 1.1) can be divided into two half-reactions.

The two half-reactions in the HyS cycle are the electro-oxidation of SO_2 at the anode and the electro-reduction of H^+ at the cathode. The half reactions can thus be summarised as: [3,26]

							ΔE (eV)	
2SO_2	+	$4\text{H}_2\text{O}$	$\rightarrow$	$2\text{H}_2\text{SO}_4$	+	2H_2	Anode	+0.316
$2\text{H}_2\text{SO}_4$			$\rightarrow$	2SO_2	+	$2\text{H}_2\text{O}$	Cathode	+3.341
$2\text{H}_2\text{O}$			$\rightarrow$	2H_2	+	O_2	Nett-reaction	+3.025

The net Gibbs free-energy required for the H_2O splitting reaction, at the anode is therefore +0.316 eV. Since H_2O splitting alone requires a significant amount of energy, the use of fuel cells with suitable catalysts are important for the production of H_2 . In general the electrical energy required in the HyS cycle can be provided by numerous alternatives to fossil fuels, such as solar energy, wind as well as solar thermoelectric generators [27]. Despite the fact that the HyS cycle serves as a viable source of H_2 as an energy carrier, its precise behaviour and properties with respect to the mechanistic pathway, are not yet fully understood [28].

The necessity of cleaner energy sources has led to the development of catalysts to reduce toxic pollutant emission and enhance combustion efficiency. In addition, as noted in Chapter 1, the necessity of more efficient and durable catalysts in the HyS cycle has contributed towards the development of SO_2 poisoning-resistant metal catalysts with a higher durability and a larger surface area per mass ratio [29,30].

The need to understand the HyS process in full becomes clear upon closer observation of the catalyst being employed. Notable is that the catalyst and electrode efficiencies, in particular within the HyS cycle, are often lowered by impurities, such as sulphur compounds. Understanding the behaviour of SO_2 on the Pt electrode surface is complicated further by co-adsorption of other S species obscuring, in particular, the experimental study of the adsorption of single species such as the adsorption of SO_2 [28]. Furthermore, the adsorption behaviour is influenced by other factors such as the variation in operating temperature (T) of the catalyst since, T also influences the dominant species present at the catalyst surface [31]. For instance, H_2O vapour, which may react with co-adsorbed species such as SO_2 , is T dependent and may influence the formation of H_2SO_4

on the catalyst surface, i.e. the reaction kinetics may show a dependency of the temperature of the $\text{H}_2\text{O}_{(l)}$. In particular, the operation temperature of the electrochemical step in the HyS cycle is normally between 350 K and 400 K, whereas the thermochemical decomposition occurs at ~ 1200 K [3].

In addition to the detrimental environmental and health effects of SO_2 , the reduction of the catalyst efficiency poses a significant problem [16,17,19,31–34]. S contaminants have, in particular, an adverse effect on Pt catalysts by affecting both the oxygen reduction reaction (ORR) and the hydrogen oxidation reaction (HOR) processes [16,29]. These adverse effects are due to active site blocking by adsorbed SO_2 and subsequent catalyst deactivation [34].

In addition to metal-adsorbate interaction, adsorbate-adsorbate interaction influences the efficiency of catalytic processes as well. In the case of SO_2 , attractive interactions among co-adsorbed species ($\text{FCC-S}_{\text{b}}, \text{O}_{\text{a}}$ adsorbed SO_2 and $\eta^1\text{-O}_{\text{b}}$ adsorbed OH or H_2) have been noted. However, these interaction energies are comparatively small (~ 0.06 eV) [35]. As a result, the behaviour of SO_2 is influenced to a certain extent by the presence of co-adsorbed OH and O_2 [35]. Since attractive interactions are observed for SO_2 , it acts as a poisoning species on catalyst surfaces wherein metal- H_2O interaction is required for the formation of H_2 .

The influence of SO_2 adsorption on metal catalysts becomes apparent when the electronic properties of the system are observed. The adsorption of SO_2 on transition metal (M) surfaces, such as Pt, may induce a charge transfer process wherein electrons are transferred from the Pt to the adsorbed SO_2 [36].

In terms of the electronic effects of adsorbed SO_2 on Pt, it has been found that a significant Pt 5d state density decrease is induced by SO_2 and S adsorption depending on the type of adsorption that occurs. The type of adsorption, however, can in turn, influence other processes such as H_2O splitting on the Pt surface [19,37].

SO_2 adsorption on Pt electrodes is weakened when applying an external electric field [35]. The recovery of Pt catalysts which have been poisoned by SO_2 is, however, still proving to be a challenge due to the increase in kinetic loss of Pt as a result of SO_2 adsorption [16,33,38,39]. In addition, catalyst poisoning due to SO_2 adsorption, which decreases Pt electroactive sites, is still a cause of concern [18].

2.2 Adsorption of other sulphur oxides

Apart from SO_2 , other sulphur oxides also pose as potential poisoning species on catalyst surfaces. The most common oxides that can be formed are SO_3 and SO . Ionic sulphur oxides, such as SO_4^{2-} and SO^+ , may be potential adsorption products as well.

In addition, the oxidation of the Pt catalyst itself can occur, given that the reaction conditions are favourable [40]. Moreover, corrosion of Pt catalysts by H_2SO_4 due to the presence of H_2O and O_2 during the adsorption of SO_2 , also poses a problem towards catalyst longevity [18].

2.3 Co-adsorption of SO_2 with H_2O and O_2

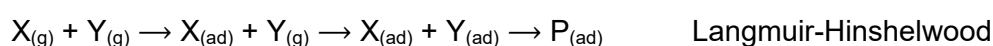
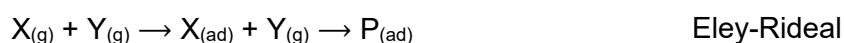
With regards to co-adsorption of multiple molecules, earlier work has indicated that SO_2 adsorption on metal surfaces may occur either localised or delocalised. In the case of a silver $\text{Ag}(110)$ surface, it was seen that if pre-adsorbed oxygen, O_{pad} , is present on the surface, SO_2 reacts with O_{pad} , at $T = 241 \text{ K}$, and subsequently forms SO_3 , which in turn undergo a self-redox reaction when T is increased to 500 K to form SO_2 and SO_4 [18,41]. This supports the observation that SO_2 adsorption is significantly influenced by both the identity and oxidation states of the metal and pre-adsorbed species. In addition, it has also been found that all complexes that have reversibly bound M-SO_2 bonds react with O_2 to form bidentate complexes [42]. The reversibility of the M-SO_2 bond is of significance in electrode recovery, since the removal of reversibly bound SO_2 requires less effort.

It has been reported that moisture minimises the poisoning effect of bisulphates in proton exchange membrane fuel cells (PEMFC) [16]. The correlation between moisture content and electrode recovery time has been studied and indicates a decrease in catalyst recovery time at high relative humidity values close to saturation [16]. Thus, the influence of H_2O , in addition to bisulphates on electrodes, is a further reason for investigation.

Furthermore, studies regarding the effect of SO_2 poisoning on the adsorption of H and OH on Pt surfaces, found that the OH adsorption process is influenced stronger by the presence of co-adsorbed SO_2 when it is compared to the degree to which SO_2 is influenced by co-adsorption with H [29].

It has been shown that pre-adsorbed oxygen (O_{pad}) enhances SO_2 adsorption and oxidation to higher oxidised SO_x species on Pt surfaces [6,18,36,43,44]. O_{pad} has also been found to increase the energy difference between the symmetric and asymmetric S-O stretching frequencies ν_{sym} and ν_{asym} , which may, as a result, influence further reactivity of adsorbing sulphur oxides [18]. During the adsorption process, a net negative charge transfer to O_{pad} from the $\text{Pt}(111)$ surface

has been observed, which can be ascribed to the strong electronegativity of O [45]. Therefore, adsorption of O has a significant influence on the further adsorption of SO₂ since O_{pad} weakens the bonding interaction between Pt and SO_{2(g)}. The weakening of the interaction between Pt and SO_{2(g)} can influence whether or not SO₂ oxidation occurs on the Pt surface and influences if either adsorbed SO_{3(ad)}, adsorbed SO_{4(ad)} or an SO_{3(ad)}-SO_{4(ad)} mixture is formed [6]. Furthermore, it has been proposed that SO₂ bonding with O_{pad} on Pt is not spontaneous and follows an Eley-Rideal mechanism [6]. In general, the Eley-Rideal and Langmuir-Hinshelwood mechanisms for the reaction between two species X and Y, leading to the formation of the adsorbed reaction product P, in the presence of a metal catalyst M, can be illustrated as [46]:



In the Eley-Rideal mechanism, one reactant is adsorbed on the surface whereafter the second reactant reacts directly from the gas phase with the adsorbed species. In the Langmuir-Hinshelwood mechanism however, both reactants are adsorbed on the metal surface before a reaction between the two occurs. Therefore, the Langmuir-Hinshelwood mechanism consists of more individual steps than the Eley-Rideal mechanism.

Since the Eley-Rideal and Langmuir-Hinshelwood mechanisms differ significantly in terms of the phases of the various reactions, the favoured mechanism will be highly dependent on the adsorption energies of the reactants on the particular metal surface. Furthermore, since the HyS cycle involves heterogeneous reactions, the Eley-Rideal and Langmuir-Hinshelwood mechanisms are of significance.

2.4 Adsorption and surface-coverage effects

An important factor influencing adsorption of multiple molecules on a surface is the number of molecules already adsorbed on the surface. The effect that several co-adsorbed molecules have on gas molecules that are in the process of being adsorbed is collectively described as the surface-coverage effect. Further aspects of the surface-coverage effect, in addition to the number of adsorbed species on the Pt surface, are the specific identity and arrangement of the pre-adsorbed species on the surface. The identity of the pre-adsorbed species is of significance where polar molecules such as SO₂ and H₂O are adsorbed. Herein, dipole-dipole interactions increase with an increase in surface-coverage.

Moreover, a linear correlation between the d-band centre lowering of a metal and the O surface coverage for various nanoparticle sizes has been observed [30]. The lowering of the d-band

centre has, as a result, been proposed as the reason for the observed decrease in adsorption energy when the O coverage is increased [30]. In contrast to the linear dependency of the d-band centre, a non-linear correlation between O surface coverage and adsorption energy per O atom has been observed for Pt nanoparticles in which higher O coverages display greater energy differences [30].

The adsorption energy decrease, which occurs during an increase in surface coverage, has been ascribed to interaction between the adsorbates. In addition, this has been ascribed to a weakening of Pt-adsorbate interaction resulting from changes in the electronic structure of the Pt surface [30].

Moreover, a Pt-S_a bond-forming (Figure 2.1b) adsorption has been observed to have a bonding preference over Pt-O_a bond-forming (Figure 2.1a) adsorption of SO_{2(ad)} [47]. In addition, stabilisation of S-bonded SO₂ is greater than that of O-bonded species [45]. It has also been observed that adsorption in which Pt-S bonds are formed tend to occur in such a way that the maximum amount of Pt atoms are coordinated to a single adsorbed S-atom, i.e. wherein S acts as a bridge between multiple Pt atoms [45].

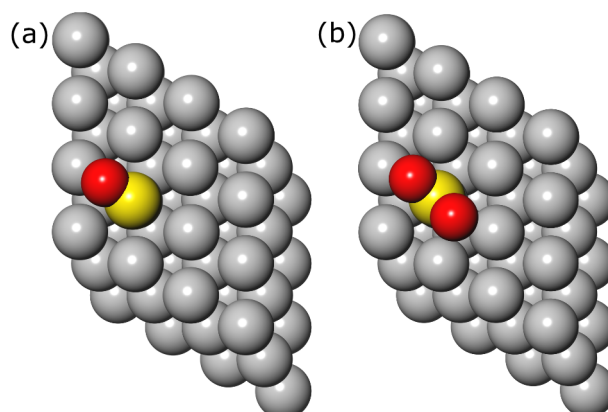


Figure 2.1: (a) O_a and (b) S_a adsorbed SO₂ on Pt(111)

Furthermore, for PEMFC operating at higher T, S compounds that are adsorbed to the Pt surface tend to oxidize at higher potentials to form SO₄²⁻, which subsequently desorbs more easily from the catalyst surface [16,31]. Furthermore, the surface-coverage can be expressed as the fractional coverage of an adsorbed species on the surface, for instance, a 25% surface coverage of an adsorbed species L, on a metal surface M, can be written as 0.25ML.

2.5 Adsorption modes and favoured adsorption sites of sulphur oxides

In terms of the adsorption mechanism, DFT studies of SO₂ adsorption on Pt surfaces have indicated that SO₂ is molecularly adsorbed in two general geometry groups. These geometry

groups are characterised by two different energies, and the end limits of the two groups correspond to SO_2 molecules which are either parallel or perpendicularly adsorbed onto the Pt surface [6,44,45]. Perpendicular adsorbed geometry is primarily formed in the case where the S atom (Pt-S-Pt) or the two O atoms (Pt-O-O-Pt) act as a bridge between Pt atoms [45].

IR and X-ray photoelectron spectroscopy studies have shown that the perpendicular:parallel adsorbed SO_2 molecule ratio has a temperature dependency, with parallel adsorbed SO_2 molecules being dominant at lower T (Figure 2.2) [6,44]. An increase in the perpendicular orientated SO_2 molecules occur, however, when the sample is heated [6,44]. Discrepant studies have, however, found that the perpendicular:parallel SO_2 ratio is, in the absence of any pre-adsorbed oxygen, more or less equal to 1:1 for surface coverages ≤ 0.25 ML [44]. Furthermore, in addition to differences regarding dominant bonding orientation, discrepancies regarding adsorption and desorption mechanisms still exist from previous investigations [6,18].

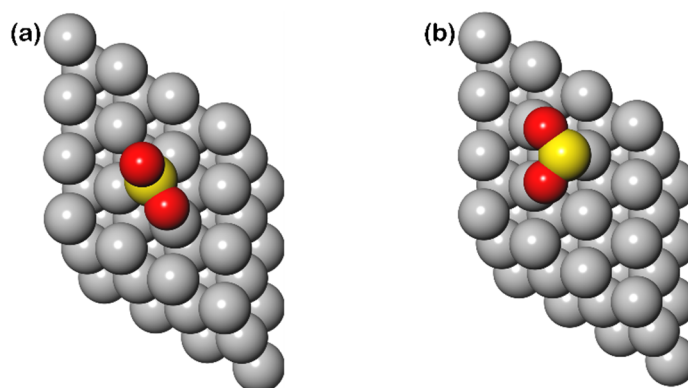


Figure 2.2: Examples of perpendicular (a) and parallel (b) adsorbed SO_2 on Pt(111)

In general, four different available adsorption sites are present on a pristine Pt(111) surface: HCP and FCC 3-fold sites, 1-fold atop sites and 2-fold bridge sites as illustrated in Figure 2.3 [45].

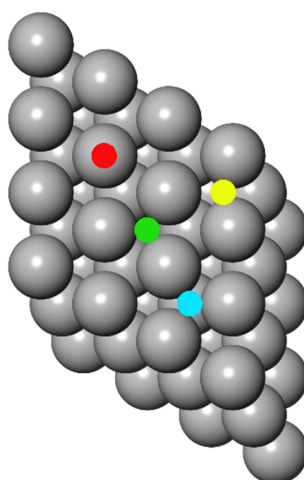


Figure 2.3: Different possible adsorption sites on Pt(111) namely FCC (green circle); atop (red circle); HCP (teal circle) and bridge (yellow circle)

It has, furthermore, been found that FCC sites have, in all cases, the more strongly bound SO_2 adsorbates compared to the corresponding HCP sites and have been ascribed to an inherent Pt(111) FCC preference [45]. This trend on Pt(111) has been observed for other adsorbate species, such as atomic S and O, as well [48].

Since the four general SO_2 adsorption modes, i.e. parallel, co-planar, bridged, O-bonded and S,O-bonded, have different adsorption energies, the adsorption orientation will also influence further adsorbate-adsorbate interaction as well as the probability of co-adsorption with other species. If some adsorption modes are significantly higher in energy than others, the probability of adsorption in the former may be negligible. Furthermore, since the adsorption energy and the probability of the different adsorption sites on a metal surface differ, it can be expected that the $\text{SO}_{2(\text{ad})}$ oxidation potential will also differ for the different adsorption sites.

It has been shown that in addition to influencing adsorption energetics, the orientation of adsorbing SO_2 molecules are influenced by other molecules, whether it is SO_2 or any other co-adsorbed species such as H_2O or O_2 , already adsorbed upon the metal surface [6]. In addition, regarding further stereochemical behaviour, it has been found that 2- and 3-coordinated ($\eta^2\text{-S}_b\text{O}_a$ and $\eta^3\text{-S}_a\text{O}_a\text{O}_a$) configurations, as illustrated in Figure 2.4, are the most stable in the case of FCC adsorption (subscripts _a, _b, _f and _h indicate atop, bridged, FCC and HCP adsorption sites, respectively) [45].

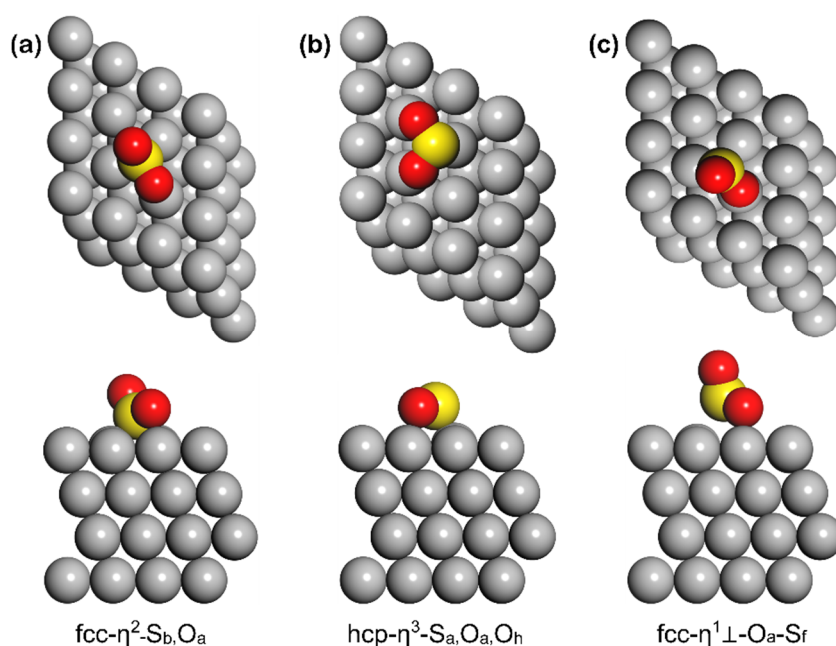


Figure 2.4: Some SO_2 adsorption geometries (a) $\eta^2\text{-FCC-S}_b\text{O}_a$; (b) $\text{HCP-}\eta^3\text{-S}_a\text{O}_a\text{O}_h$ and (c) $\text{FCC-}\eta^1\text{-O}_a\text{Sr}$ possibilities on Pt(111) with the adsorption site of each atom marked with subscripts

Several internal structural changes have been observed to occur in the adsorbate molecules during the adsorption process. A smaller O-S-O bond angle for SO₂ wherein all three atoms are directly bonded to the Pt surface is observed in comparison to adsorption where one O atom is not directly bonded to the Pt surface [28]. This difference in bond angle has been ascribed to a difference in geometric constraints between the two orientations of the adsorbed SO₂ [28].

Similar to SO₂, a tendency towards favouring FCC adsorption sites are displayed by both SO and SO₃ on Pt surfaces as well [28]. FCC- η^3 -S_a,O_a,O_a adsorbed SO₃ has been shown to be the most stable, being related to the parallel adsorbed FCC SO₂ [28]. Moreover, a close relationship between surface bonding SO₃ FCC- η^3 -S_a,O_a,O_a and SO₂ FCC- η^3 -S_a,O_a,O_a has been suggested [28,45].

Similar to FCC- η^3 -S_a,O_a,O_a adsorbed SO₃, it has been found that chemisorbed SO₃, adsorbed as FCC- η^3 -O_a,O_a,O_a has a strong bond with the Pt surface [28]. In contrast, sharing of metal atoms among S and O (therefore Pt bridging SO species) has been found to weaken the adsorption bond strength significantly ($E_{\text{ads}} = 0.131 - 0.148$ eV for η^3 -S_b,O_b,O_b vs $E_{\text{ads}} = 0.918 - 0.926$ eV for η^3 -S_a,O_a,O_a) [45]. In addition, it has further been suggested that S atoms adsorbed on bridged sites of Pt(111) have a higher mobility than atop sites and furthermore, that these atoms are more easily desorbed from the Pt(111) surface via the reformation of S₂ [19].

Bonding interactions between S and Pt have been found to differ significantly for hollow (i.e. FCC and HCP) sites compared to bridged adsorption sites and have been ascribed to a greater negative charge on the S atom when adsorbed at hollow sites [19]. As a result of these differences in interaction, bridged site S_b adsorption has a greater Pt work function increase than in the case of the hollow site (FCC and HCP) S adsorption [49]. These differences in work functions are also found to occur for other transition metal surfaces such as Ru(III) [49].

In general, proposed overall mechanisms for SO₂ adsorption on Pt are described primarily either as a dissociative adsorption mechanism, as SO⁺ and O⁻ or SO and O or as intact-adsorption (molecular) as SO₂ [18]. A dissociative adsorption mechanism has been proposed for low surface coverage, whereas a higher coverage is accompanied by non-dissociative (or molecular) adsorption [18]. This preferred adsorption mechanism will inherently influence the oxidation preference of the adsorbed molecules towards Eley-Rideal or Langmuir-Hinshelwood mechanism as described in §2.3 p.9.

2.6 Factors influencing SO₂ adsorption on Pt surfaces

The adsorption and oxidation of SO₂ on Pt surfaces are influenced by various factors. Therefore, all these factors should be considered within the adsorption studies. Among these factors are the identity of the metal species, the possible presence of pre-adsorbed species on the surface, the polarity of the adsorbates, as well as environmental variables such as temperature. In particular, the presence of co-adsorbed species on the metal surface inherently influences both the reaction mechanism as well as the reaction products that SO₂ forms on the metal surface, in this case Pt.

The presence (or absence) of co-adsorbable species, such as H₂O and O₂, on the surface influences the availability of different adsorption sites upon which adsorption can occur. Since co-adsorbed species inherently affects the electron distribution on metal surfaces, the adsorption of new gas molecules will influence the energy and stereochemistry of the adsorption process. Moreover, as soon as many adsorbed species are present on a metal surface significantly strong interaction between adsorbates and near-positioned gas species may occur and is in general described as the surface-coverage effect of the adsorbates.

The importance of the specific identity of the pre-adsorbed species becomes clear when the behaviours of adsorbed atomic S and atomic O are compared. Atomic S has a observably different binding behaviour than atomic O_{ad} ($\mu_d = -0.2$ D) on Pt(111) with different properties such as the fact that S has a positive dipole moment ($\mu_d = 0.4$ D). Subsequently, S also has a different polarisation ability, and thus differ in susceptibility towards co-adsorption with other co-adsorbates [45]. Furthermore, dipole-dipole interactions have been, at ≤ 0.25 ML coverage, responsible for lateral repulsion between SO_{2(ad)} molecules, which contributes to surface activity as well as surface adsorption capability [45].

When other co-adsorbing species apart from oxygen are observed, various differences in their co-adsorption behaviours are noted. An example is the case wherein co-adsorption of SO₂ and H₂ occur. In contrast to the SO₂ susceptibility of H adsorption, SO₂ adsorption on Pt is found to be insignificantly affected by co-adsorbed H and furthermore that SO₂ is not desorbed from Pt as a result of H co-adsorption [50]. This insusceptibility of SO₂ has been ascribed to a higher stability of adsorbed S and sulphur oxides on Pt than adsorbed H [50].

2.6.1 The influence of temperature

Another influential factor on the SO₂ adsorption mechanism is the temperature (T), which in turn also influences the oxidation of SO₂ to SO₃²⁻ and SO₄²⁻ [17]. From the kinetic theory of atoms and solids, the reactivity of metal catalysts can be influenced by temperature as well, since the interaction between the metal and adsorbate atoms is required in catalysis.

Studies have found that a higher T enhances the oxidation of SO₂, to SO₃ and SO₄, given that there is a sufficient O₂ supply, and that SO₄ is the only stable SO_x species at very high T [6,28,36]. Furthermore, a step-wise SO₂ oxidation reaction, wherein various intermediate species are formed with increasing T, has been proposed [6]. It has additionally been found by further studies that the oxidation of SO₂ to SO₄ may take place both with or without the formation of SO₃ as an intermediate product [18].

It has been shown that SO₂ chemisorption on Pt(111) at very low T (< 160 K) leads to the formation of two distinct T-dependent surface species both of which undergo S desorption as SO_{2(g)} [18]. It has also been found that for T > 300 K SO₂ oxidation occurs on an O-pre-covered Pt surface to form chemisorbed SO₄ [18]. However, nearly-upright standing SO_{2(ad)} on Pt(111) has shown not to form SO₄ when heated to 300 K and has been ascribed to a coverage effect which prevents oxidation [51]. It has furthermore been concluded that a lower amount of adsorbed atomic S_(ad) is left on the Pt surface when a mono-layer SO₂ system is heated in comparison to heating a multi-layered SO_{2(ad)} system [51].

Multi-layered SO_{2(ad)} has been observed to undergo desorption when T is increased to 130 K, whereafter a single upright-standing SO₂ molecule layer is left on the Pt surface [51]. This single SO₂ layer has, furthermore, been observed to undergo desorption as well when the surface is further heated to 285 K [51]. Even further heating of the system can result in SO₂ decomposition and subsequent formation of atomic S and atomic O as well, of which the latter can produce SO₄ after further reaction with monolayer SO₂ occurs [51].

The decomposition of SO_{4(ad)} upon heating has systematically been described as SO_{4(ad)} → SO_{2(g)} + O_{2(ad)} [51]. This result for mono Pt-SO_{2(ad)} systems is similar to observations for other mono Pd-SO_{x(ad)} systems [51,52]. It has additionally been observed that decomposition of SO₄ takes place at 418 K without resulting in an increased amount of adsorbed atomic S_(ad) on the Pt surface [51].

It has been found, from temperature-programmed desorption (TPD) and mass spectrometry studies, that the bonding energy between Pt(111) and SO₂ is 100-150 kJ·mol⁻¹ [53]. This binding energy is, however, for the bond formation between SO_{2(ad)} and a pristine Pt(111) surface and is consequently changed, due to an increase in adsorbate-adsorbate interaction, as the adsorption sites become more populated by SO₂, i.e. a surface-coverage effect. This change in bonding energy becomes clear when the influence of S coverage on SO₂ adsorption is studied. Herein the adsorption energy between Pt(111) and SO₂ is significantly lower than that of S at ½ coverage of the Pt(111) surface [28].

2.6.2 Neutral and ionic sulphur oxides

In cases wherein SO_3 is indeed formed, a geometry transformation occurs by the oxidation of SO_2 to SO_3 . Similarly, a change from desorbed $\text{SO}_{3(g)}$ to the SO_3^{2-} ion also brings forth a further geometry transformation, in this case, from planar to pyramidal [36]. In addition, the frequencies of the S-O stretching vibration, and thus the S-O binding energies, are also influenced by the geometry in which SO_3 is bonded to the metal surface [18]. Furthermore, the occurrence of frustrated (thus in which molecule movement is constrained to specific directions) rotation, translation, vibration and in- and out-of-plane bending movement of adsorbed SO_2 on Pt surfaces can occur, through which both SO_2 adsorption and oxidation energies are further influenced [54].

2.7 Structural properties of adsorbed sulphur oxides

Several structural changes, as summarised in Table 2.1, occur within sulphur oxides during adsorption onto a Pt surface.

Table 2.1: Structural properties of the most stable adsorption geometries of some adsorbed sulphur oxides, reported in literature

Sulphur species	Adsorption Geometry	Property			
		$d(\text{S-O}(1)_a)$ (Å)	$d(\text{Pt-S})$ (Å)	$d(\text{S-O}(2)_a)$ (Å)	$d(\text{S-O})$ (Å)
SO_2	FCC- η^2 - S_bO_a	1.54 ^a ; 1.47 ^a	2.31 ^a		
SO	FCC- η^1 - S_f		2.27 ^a		1.47 ^b
SO_3	FCC- η^3 - $\text{S}_a\text{O}_a\text{O}_a$	1.56 ^a		1.56 ^a	1.46 ^a
S	FCC- η^1 - S_f		2.34 ^c		

a: Lin et al. 2002 [45]; b: Happel et al. 2011 [6]; c: Rodriguez et al. 1996 [19]

A shorter adsorption bond length (2.27 Å) for adsorbed SO_2 (on Pt(111)) has been observed than for adsorbed atomic S (2.29 Å) [28]. Furthermore, a longer bond length in parallel adsorbed SO_3 has been observed in comparison to SO_4 and up-right SO adsorbed species [6]. In contrast, atomic FCC- O_{ad} has a shorter Pt-O bond length (200 pm) compared to the Pt- O_a bond length in PtSO_2 (FCC- η^2 - S_bO_a) (2.30 Å) [45]. Inherently, from the definition of dipole moment, a shorter bond length tends to lead to a subsequent increase in the perpendicular dipole moment ($\mu_{d\perp}$) of the adsorbate system [45]. In contrast, only small $\mu_{d\perp}$ values for parallel adsorbed geometries, such as η^3 - $\text{S}_a\text{O}_a\text{O}_a$, have been observed [45]. An intermediate negative $\mu_{d\perp}$ value has, however, been observed for the perpendicular and marginally tilted S dominant SO configurations, such as η^2 - S_aO_b [45]. In addition, $\mu_{d\perp} \gg 0$ has been observed for the $\text{SO}_{2(ad)}$ η^2 - O_aO_b configurations [45]. The importance of the value of μ_d becomes apparent from its particular influence on the adsorption energies and geometries of possible adsorption modes at any particular T, which subsequently influence the catalyst efficiency as well. Chemisorption of a SO_x molecule onto a metal surface tends to increase the internal S-O bond lengths due to a reduced bond strength induced by the

metal surface atoms [28,45]. For the η^1 -SO₂ FCC adsorption mode, however, an increase in bond strength has been proposed by an observed increase in the S-O stretching frequency that occurs [28].

Among the primary SO₂ adsorption configurations on Pt(111), SO₂ FCC- η^2 -S_bO_a and atop η^1 -S_a(O_a)₂, have been found to be the most stable and unstable adsorption modes, respectively [6,45]. The latter, as well as bridged η^1 -S_b(O_b)₂ adsorbed SO₂, relax to the η^1 -S_f(O_f)₂ configuration when an optimisation is performed [28]. Additionally, a binding energy increase of 2.982 eV due to a configuration change from FCC- η^1 -O_f(S_f) to FCC- η^1 -S_f(O_f) has been observed, which is further indicative towards the S-bonded adsorption preference on Pt [28,45].

Similar to the adsorption properties of SO₂, SO wherein the O is directly bound to the metal, such as in the case of FCC- η^3 -S_aO_aO_a, has been found to have the greatest surface-perpendicular dipole moments [28]. These observations support the favourable SO_x adsorption geometry on FCC sites, wherein the S atom is directly bonded to three Pt surface atoms [28]. Furthermore, although SO_{3(g)} has a trigonal planar structure, studies have found that adsorption onto Pt surfaces induces a structural change to trigonal pyramidal SO_{3(ad)} with the S no longer sharing the same plane as the three O atoms [28]. In addition, nearly-planar SO₃ species have been found to have the lowest adsorption energies [28]. As with SO₂, it has been found that adsorbed SO₃ is bonded stronger at FCC than HCP sites [45]. These adsorption differences have been ascribed to the FCC preference of the ground state Pt(111) [45].

Two adsorbed SO₂ species have been identified by high-resolution photoelectron spectroscopy (HR-PES) on Pt(111)-O_{pad} with bonding energies similar to pristine Pt(111) covered by perpendicular and parallel adsorbed SO₂ (see Figure 2.2 p.12) [6,51]. Furthermore, perpendicular SO_{2(ad)} has been found to be more stable than parallel adsorbed SO_{2(ad)}, consequently, also affecting the further oxidation ability of the adsorbed species [6].

Diffusion by adsorbates between different adsorption sites, such as from HCP to bridged sites, also has an influence on the further adsorption of co-adsorbed species on the Pt surface [30]. In particular, for a given adsorbate, when the adsorption energy-difference between the different adsorption sites is relatively small, diffusion on the Pt surface can occur readily and to a greater extent, with subsequent co-adsorption thus having a higher probability to occur [30]. An example is the adsorption of O₂. Herein, an adsorbate mobility difference between different Pt facets such as the Pt(111) and Pt(100), has been observed, and that destabilisation of O₂ on HCP (111) site edges occurs when an increase in O₂ coverage takes place [30].

Despite all of the aforementioned conclusions regarding the adsorption of sulphur oxides on Pt surfaces, the mechanisms of catalyst inhibition reactions by sulphur compounds, particularly where chemisorption occurs, are not fully understood [17,54]. The necessity to understand these reactions and processes become apparent since blocking of electro-active sites on catalysts decreases both catalyst efficiency and sensitivity [15,17,33].

In comparison to SO, SO₂ and SO₃, tetrahedral SO₄ (FCC- η^3 -O_a,O_a,O_a) has the smallest number of possible binding orientations and has been described as being the most stable adsorbed SO_x species [28,45]. Thus far, the best description of adsorbed SO₄ is proposed as being SO₃ which is weakly bound to an O atom that is covering the Pt surface [28]. Furthermore, the fact that SO₄ has the greatest amount of resonance structures contributes to the stabilisation of the Pt-SO₄ adsorbed system. In addition, some high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) studies have indicated that highly stable SO₄ is formed on the Pt(111) surface where pre-adsorbed O_{pad} is present [18,28]. Tridentate SO_{4(ad)} has been observed as being lower in energy on Pt surfaces than mono- and bidentate SO_{4(ad)} and that the latter are destabilised with respect to the tridentate SO_{4(ad)} [6].

In addition to Pt, multi-layered SO₂ adsorption has also been reported on noble metals without the formation of secondary compounds such as sulphates [36]. Studies on metal catalysts showed that SO₂ is desorbed at low T (< 380 K) and that only partial oxidation of SO₃²⁻ to form SO₄²⁻ occurs [36]. It has also been found that heating the system above the SO₂ adsorption range (T > 550 K) leads to an increase in S oxidation state from S⁴⁺ to S⁶⁺ (in the form of adsorbed MSO₄) [18,36]. Further heating can, in the case where SO₄ is also bonded as a ligand, change SO₄ from bonding as a mono- to bidentate ligand, thus also influencing adsorption and (E_{ad}) desorption energies [18,36]. Further studies have shown that adsorbed SO₂ on d⁸ and d¹⁰ transition metal complexes is, in general, eliminated upon heating which subsequently acts as a Lewis acid [42]. It has also been proposed that in most cases, a correlation between coplanar orientation and non-reversible SO₂ binding exists [42]. In contrast, it has been proposed under favourable circumstances that SO₂ may reversibly bridge two M atoms in which M-M bonding is involved [42].

2.8 Electronic properties of adsorbed sulphur oxides

Adsorption of gas molecules on Pt(111) can in addition to structural changes, be accompanied by changes in the electronic structure, i.e. the distribution of electrons. Both forward and back donation of electrons (e⁻) can occur when SO₂ is adsorbed onto a Pt surface (depending on the surface-bound atoms of SO₂), through which both the adsorption energy and e⁻ density can further be influenced [45].

First-order bonding effects by species in close proximity to the adsorbate, such as near-lying surface Pt atoms and neighbouring adsorbate molecules, have a significant influence on the bonding nature of a given adsorbate molecule X [45]. Furthermore, E_{ad} is also affected by second-order bonding effects which result from the influence of orbitals of non-surface bulk Pt atoms which are not in direct contact with the adsorbed $SO_{2(ad)}$ [45,55].

It has been proposed that the S of SO_2 provides the greatest contribution to the back-donation of the Pt- $SO_{2(ad)}$ system in which an e^- is donated from the Pt 5d (HOMO) to the unoccupied $SO_{2(ad)}$ (LUMO) orbitals [45]. Moreover, a significant broadening of SO_2 frontier orbitals in the metal d-band region, together with a large low-lying orbital resonance and a small unoccupied b1 above the Fermi level, have been qualitatively proposed as requirements for sufficient bonding between Pt and SO_2 to occur [45]. In addition, the bond-formation between Pt and SO_2 orbitals has been described as covalent rather than ionic in nature [6]. The covalent bonding nature may thus contribute to the relatively weak physisorption that is observed.

Studies regarding mono layer SO_2 coverage on Pt have indicated that eight to ten Pt atoms can be blocked by one or more adsorbed S and that a negative charge resides on the adsorbed S, which as a result, significantly decreases catalyst reactivity particularly with respect to H_2 adsorption [37,50].

In terms of catalyst surface structure, it has been found that for a low relative S content, that the Pt-H bonds on Pt(111) are affected to a greater degree than on Pt(110) [50]. Electrochemical and spectroscopic studies have indicated that O_2 is permanently absorbed by S adsorbates on Pt when H_2SO_4 electrolyte solutions contain sufficient traces of atmospheric O_2 [37]. It has been found that for Pt vulcan electrocatalysts, a 33% decrease of Pt mass-activity and an ORR rate-decrease can be caused by a 1.2% S adsorption coverage onto the Pt catalyst and that it furthermore increases the rate at which peroxides are formed [29,31]. As a result, severe damage can be caused to the catalyst surface by the formation of peroxides [31].

From studies specifically regarding surface coverage, it has been found that a 14% S coverage on a Pt catalyst surface is able to lead to a 95% depletion in Pt mass activity [31]. Furthermore, Pt- SO_2 adsorption energies are significantly affected by the type of surface site onto which SO_2 is adsorbed, i.e. the surface orientation with respect to SO_2 [29]. Therefore, the availability of specific adsorption sites will influence not only the energy of initial adsorption, but also the arrangement of adsorbates on the surface when co-adsorption takes place.

In general, the electronic, coverage and bonding influence of adsorbed SO_2 on Pt, can be investigated and clarified by means of charge density methods such as Bader Analysis.

2.9 Adsorption on Pt alloys

A distinct correlation between SO_2 poisoning susceptibility and the identity of the metal catalyst has been observed [29]. It has furthermore been found that alloyed catalysts, such as Pt-Pd and Pt-Ni catalysts are more resistant to S poisoning than pure Pt, Pd and Ni catalysts [29,56]. In addition, a stronger adsorbate-Pt(111) surface interaction has been observed than for Pt-Ni alloy interaction for the same adsorbate species [29]. The stronger resistance of the alloy catalyst has been correlated with a lower d-band centre for the Pt-Ni alloy than in the case of pure Pt metal [29]. Furthermore, studies have found that at relevant fuel cell potentials the catalytic activity on $\text{Pt}_3\text{Ni}(111)$ for the ORR is the highest of all cathodes used in this process being significantly more reactive than the Pt(111) surface [56].

Work wherein catalysts consisting of pure metals are compared to catalysts consisting of alloys, found that poisoned Pt_3Ni alloyed catalysts are more easily cleaned and recovered than in the case of mono Pt catalysts [29,56]. Although a greater d-band shift, due to SO_2 adsorption, has been observed for Pt-Ni catalysts than for pure Pt, mono Pt catalysts are still poisoned to a greater extent due to various additional influential factors on the metal surface [19,29]. It has been concluded in previous papers that, due to their different poisoning susceptibilities, Pt-Ni(111) and Pt-Pd bimetallic catalysts serve as significantly superior ORR catalysts than pure Pt(111) [29,56].

In addition, it has been found that adsorption on poisoned Pt sites is further influenced by, among others, the influence from the Pt d-band shift [29]. A significant depletion of the Pt d-band population is induced by SO_2 adsorption, thus also decreasing the Pt catalyst reactivity towards the HyS process [19]. Moreover, it has been found that under certain circumstances the relationship between the d-band energy and OH adsorption energy is not linear thus reducing the accuracy of the d-band centre as a quantitative catalyst adsorption indicator [29]. A complication that arises with regards to the SO_2 adsorption difference between Pt and Pt-alloys is that despite the fact that SO_2 adsorbs stronger to Pt than to for example Pt-Ni alloys, Pt oxides are oxidised to a greater extent than Pt alloys and that the oxidised adsorption sites are subsequently blocked to a greater extent against further SO_2 co-adsorption [29]. However, since alloys are beyond the scope of this dissertation, it will not be discussed in further detail.

2.10 The influence of SO_2 adsorption on the electronic properties of metals

Previous papers have indicated that the degree of chemisorption of atomic oxygen adsorbates on metal surfaces depends significantly on the valence electron structure of the metal involved [4,18]. In general, a greater extent of chemisorption of atomic oxygen occurs with early d-metal ions (d^1 , d^2 and d^3), in addition to forming the strongest bonds in the case of the first transition

metal series (3d), in comparison to the second (4d) and third (5d) series [4]. Since the metal d-states and the O 2p-states have to be, according to Pauli's principle, orthogonal in an ideal system, non-ideal overlap between M^{m+} d- and O 2p-orbitals gives an increase in bonding molecular orbital energy [4,57]. The kinetic energy (E_{KE}) of the system is, therefore, increased by an amount which is proportional to the square of the metal-adsorbate matrix element (V_{ad}^2). Thus, a greater overlap between the metal d- and adsorbate 2p-orbitals leads to a stronger repulsion [4]. The nuclear charge also influences V_{ad} with smaller V_{ad}^2 values corresponding to a higher nuclear charge (Z) [4]. Apart from the identity and oxidation state of the metal, other factors that do have an influence on V_{ad}^2 are the adsorbate itself, as well as the relative positions of the metal atoms and the adsorbate ions [4]. It has further been stated that larger matrix elements correspond to a stronger bond formation as well as an increase in the Pauli repulsion [4].

A two-step adsorption process has been proposed for the metal-adsorbate interaction, as in the case of SO_2 [30]. Firstly, a renormalisation of adsorbate s- and p-orbitals takes place due to the interaction with the metal's s- and p-orbitals. Thereafter, interactions between metal d-orbitals and the renormalised adsorbate s- and p-orbitals occur, and bonding and anti-bonding orbitals are formed with energies characteristic to the specific metal-adsorbate system [30,56].

When adsorption of molecules, such as CO_2 , H_2S and SO_2 to metal surfaces are studied, the adsorbate-surface interaction is influenced by various adsorbate valence configurations, complicating the system's behaviour [4]. Additionally, the E_{ad} , surface diffusion, adsorption and desorption kinetics on the metal surface due to attractive and repulsive interactions within metal-surface covering, can be influenced further by adsorbate-adsorbate interaction [4,45]. For instance, it has been shown that a ~ 0.17 eV adsorption energy increase for SO_2 occurs for the most strongly bound configuration when the surface coverage decreases from $\frac{1}{4}$ ML to $\frac{1}{9}$ ML [45]. When the surface-adsorbent contact region starts to be dominated by repulsive interactions, however, bond breaking can occur, leading to eventual desorption [4].

Flat-model systems have clear IR spectra with significantly distinguishable absorption peaks which are, in contrast to conventional spectra, easier to identify and interpret [58]. The formation of additional IR spectra bands when an increase in SO_2 adsorption layer thickness occurs has also been reported [6]. The interpretation of $PtSO_{2(ad)}$ IR spectra should, however, be studied with caution since some IR adsorption bands of free $SO_{2(g)}$ can be absent or weakened for adsorbed $SO_{2(ad)}$. Furthermore, the selection rule has been shown to weaken for very small adsorbed particles [59].

It has furthermore been indicated, that the adsorption strengths of S species on Pt (111) increase in the order $SO_2 < SO_3 < SO < SO_4 < S$ [6]. Moreover, an inner-layered-Pt-atom-induced decrease

in HCP adsorption energies, and in particular, in which the Pt(111)- X_{ads} distance is short, has been observed [6]. Furthermore, it can be expected that if a significantly stable Pt(111)- X_{ads} -intermediate product is readily formed during adsorption, it will be relatively resistant towards further oxidation as well as towards further reactions with co-adsorbed species. If the X_{ads} species is a strong poisoning molecule, recovery of the Pt catalyst can be complicated and prolonged.

Little is, however, known with respect to the mechanism and influencing factors by which many heterogeneous catalytic processes, and in particular SO_2 adsorbate-catalyst-surface reactions, take place [4,6]. The reason little is still known is partially due to the complexity by which heterogeneous reactions occur and although various first-principle and semi-empirical calculations of surface energies (γ) have been carried out, few mechanistic modelling studies regarding these surface reactions have been performed [58,60].

Adsorption can, in general, be classified as chemisorption or physisorption depending on the surface-adsorbent interaction [54]. In physisorption, adsorption occurs as such that no chemical bond breaking takes place and that both substrate structures remain intact [54]. In addition, the dominating interaction involved in physisorption is the weak Van der Waals forces. Furthermore, due to the weak strength of Van der Waals forces, the surface-adsorbate interaction in physisorption is much weaker than in the case of chemisorption [54]. Chemisorption, however, takes place specifically via the occurrence of chemical reactions between the metal surface and adsorbate molecules and often strongly influences catalytic activity [54].

2.11 Adsorption and molecular orbitals

Since d-states of transition metal cations (M^{m+}) are close to one another in terms of their energies, bonding (BMO) and anti-bonding (AMO) molecular orbitals are formed that are similar to a two-state system, due to the interaction between the d-orbitals and the adsorbent orbitals [4]. Similar to chemical bonding between (M^{m+}) and ligands (L^n), the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the surface-adsorbent system depends, to an extent, on the MO energies of the two involved compounds. If the energy of the surface atoms (E_{surf}) is close to the energy of the adsorbent molecules (E_X), the field stabilisation energy (E_{FS}) will be large. As a result, more adsorption onto the metal surface may occur. Thus, chemisorption can be classified as strong when split-off bonding and anti-bonding states are formed [4]. Consequently, poisoning of catalyst surfaces will often have a greater severity when chemisorption instead of physisorption takes place.

One general method by which calculations are approached is to start with a technical complex catalyst and leave out some features to simplify the initial calculation [58]. A second approach is

to begin with a single crystal to which more complex features are systematically added until the required bulk catalyst system is obtained [58]. The chosen method, therefore, depends on the calculation type that is required [58].

2.12 Describing electrons

The development of quantum mechanics has provided a better description of matter, both on an atomic and sub-atomic level. Fundamentally, quantum mechanics are largely based on the Schrödinger equation for the hydrogen atom, i.e. $\hat{H}\psi = E\psi$ in which E is the total energy of the system and $\hat{H}$ is the Hamiltonian operator [20].

Therefore, in quantum mechanics, particles are described by unique wave functions ψ containing all the relevant information regarding the movement and energy of the single-particle system. However, since the Schrödinger equation is only solvable for the H atom (i.e. 1-electron system), multi-electron systems are described with approximations. Various approximations have been developed, most of which are often utilised by molecular modelling to describe a variety of molecular systems. In general, three different approaches toward molecular modelling have been proposed, namely, empirical, semi-empirical and ab-initio methods; each having their own unique advantages and disadvantages [21].

2.13 An overview of molecular modelling theory and DFT

Molecular modelling provides a useful means to study and predict the SO₂ oxidation reaction mechanism and to develop a detailed understanding of the sulphur compound and, in particular, SO₂ chemistry such as adsorption, desorption and oxidation. Side reactions can be investigated as well to determine stable and metastable compounds that may form on Pt surfaces. Properties such as surface structure and equilibrium geometry can be calculated by molecular modelling, thus providing a more detailed understanding of surface reactions [4]. Molecular modelling also enables the studying of catalyst processes under high temperature and pressure conditions [4]. Surface reactions are, however, complex and difficult to describe due to various compounds that may simultaneously be present on the metal surface. It is, therefore, beneficial to divide surface processes into a series of elementary reactions describing different reaction products individually [4].

Molecular modelling provides a useful alternative to experimental studies with respect to saving research cost and analysis time. In general, two modelling types are used, namely, density functional theory (DFT) and molecular mechanics (MM). DFT simplifies quantum mechanics in the sense that it determines the electron density of a complex system from which several inherent

properties of the system are subsequently derived, rather than trying to solve the actual wave function of the system [61]. Thus two systems with the same electron density can be approached in similar fashion in DFT regardless of the fact that their real electron counts might differ [61].

DFT is more accurate than classical MM in describing molecules. MM is, however, simpler with shorter calculation times than DFT but not as widely applicable. DFT applicability becomes apparent in its usefulness in describing surface reactions and in the modelling of various physical reaction quantities such as chemisorption energies.

A basis set, which is a linear combination of single-electron solutions of the Schrödinger equation, can be used to approximate multi electron systems. The wave function of the real system being examined is approximated by a linear combination of individual wave functions of single-electron systems [62]. The wave function ψ , of a multi-electron system, may thus be approximated as:

$$\psi = \sum_{i=0}^n c_i \phi_i,$$

wherein ϕ_i is the wave function of the i -th electron and c_i is the mixing coefficient of the i -th electron (i.e. the contribution coefficient towards ψ).

2.13.1 DFT approximations

It should be noted that numerous approximations for multi-electron systems have been developed, either separate from (e.g. Hartree-Fock), or as a sub-division of DFT, e.g. Kohn-Sham (KS), Hohenberg-Kohn (HK), ab-initio and semi-empirical methods [63–65]. In addition, although the exact expression of the functional in the HK approximation is unknown, DFT has been used with the aim of approximating this functional with a minimum error [21].

In general, the DFT approximation describes the total electron-density $\rho(\vec{r})$ as a function of the normalised wave function of a multi electron system, i.e.:

$$\rho(\vec{r}_1) = \int \psi^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n) d\vec{r}_2 \dots d\vec{r}_n,$$

with ψ^* the complex conjugate of ψ and $\vec{r}_i$ the positional vector of the i -th electron in the ensemble.

Although semi-empirical methods are popular and accurate when small systems with small molecules are studied, it often fails to describe larger systems such as metal surfaces, sufficiently [66]. To overcome these difficulties, numerous functionals have been proposed in order to refine and improve the accuracy, and thus the usability, of DFT in large molecular systems, rather than to make use of semi-empirical methods.

2.13.2 DFT and solid-state systems

In solid-state systems, cluster and slab models form two principle methods. Herein the number of electrons used is limited to simplify calculations without compromising computational accuracy [4,58]. Since DFT methods are only approximations of the real system being described, the accuracy of the chosen model always depends on the parameters, such as computing time, convergence criteria or the chosen basis set [4].

Cluster methods use only a limited number of surface atoms contained within a chosen cluster volume [4]. In this method, it is assumed that the atoms situated far away from the surface, and therefore in adsorption systems inner bulk atoms far away from the adsorbate, do not have a significant effect on the adsorbate behaviour [4]. As a result, molecules and atoms in the bulk structure far from the surface are either negligible when calculating E_{ad} or can be replaced by a constant energy term [4]. In Slab methods, however, the material surface is described as a slab with a periodic surface structure. Since the unit cell size influences the computational effort and time needed, care should be taken when selecting the cell size. In addition, the size of the unit cell should be large enough so that adsorbates on neighbouring unit cells do not react to influence the calculated adsorption energies [4]. Thus, the decision of using either cluster or slab methods is highly dependent on both the properties of the molecular system as well as the inherent properties of the specific model being applied.

As noted, molecular modelling calculations are further influenced by the selected basis set functions. The most common types of basis sets used in molecular modelling are localised functions (atomic orbitals, Gaussian functions and linearised muffin-tin orbitals (LMTOs)) and plane-waves such as projector augmented waves (PAW) or linear augmented plane waves (LAPWs) [4,67]. In cluster models, localised functions, such as Gaussian basis sets, are often used since they are specifically localised around the atoms [4,68]. In contrast, both LMTOs, as well as LAPWs, are used in slab-type methods [4].

In order to evaluate the stabilities of reactants and products in a system, and thus the probability of a reaction to occur, their energies are measured with respect to the Fermi-level. The Fermi-level surface is often used in modelling and is defined as an imaginary surface in reciprocal space which divides occupied from unoccupied electronic states of a system at $T = 0$ K [69]. Thus, all electron energy states above the Fermi level are referred to as excited states. A wide range of techniques currently exists to determine and describe the Fermi surface of a compound [69]. In real solid-state systems, however, the Fermi surface is not spherically shaped, and consequently, the rigid band model wherein the electron density causes a rigid up and down movement of the Fermi-level, is insufficient. This deviation from a spherical structure is, among others, ascribed to

the weakening of the relationship between electron-atom ratio $e/a = 1.41$ and the body-centred to face-centred-cubic (bcc-FCC) transition in solid crystalline materials [69–71]. This deviation further enhances a trend in the system to approach the free electron model and promotes the simplification of models that are utilised for the approximation of solid-state material properties [69].

Various smearing methods have been developed in order to account for the fact that the Fermi levels of conductors and isolators differ significantly in terms of its position in the band structure. In conductors, the Fermi level is positioned in a point where there is a finite density of states whereas the Fermi level lies inside a band structure gap in insulators. As a result, the choice of smearing methods depends significantly on the conducting properties of the observed system. In general, regarding heterogeneous catalysis, the Methfessel-Paxton smearing method often describes metallic systems significantly well through its inclusion of a delta function, δ , in the Hermite functions, with $\delta = k_b T (-\ln(g))^{0.5} (\eta N)^{-1}$ [72]. Here, k_b is the Boltzmann constant, N is the order of the Methfessel-Paxton approximation, T is the temperature, $g > 0$, and η is a user defined parameter to control the fineness of each step [73].

Another method to enhance the description of solid-state systems is the employment of Bloch wave functions to describe electron movement in the crystal lattice [74]. A Bloch function describes systems of particles moving in a periodically repeating electronic environment such as in the case of crystal structures. Thus, Bloch functions are, as a result, described as functions that are a product of a plane-wave $f = e^{ikr}$ and a periodic function $u(\vec{r})$, and have the form: $\psi(\vec{r}) = u(\vec{r}) \cdot e^{i\vec{k}\vec{r}}$ [75]. In Chapter 3, the specific use of Bloch functions is described.

Wave functions, used to describe electron movement, can be described further by the wave-vector $\vec{k}$ in the imaginary (or reciprocal) k-space region. In describing electrons with molecular modelling, it is often useful to make use of a Brillouin zone to calculate molecule energies in a solid-state crystal [76]. Mathematically, the first Brillouin zone is a uniquely defined primitive cell in reciprocal space which can be occupied by two electrons (and from the Pauli exclusion principle, with opposite spin-directions) [57,69]. As a result, planes related to points on the reciprocal lattice are used to define the Brillouin zone boundaries and are used to aid in describing molecular energy levels of crystalline solids [69]. Since Brillouin regions of solid-states are chosen in such a manner as to be identical, the solutions to the wave functions of electrons moving in a periodic medium, such as a crystal lattice, can be described in full by their properties and behaviour in a single Brillouin zone. Furthermore, the Bloch wave theory also leads to the formation of band gaps at the Brillouin boundaries due to the Bragg reflection that takes place on the solid surface [69].

The accuracy and simplicity of the description of solid-state systems can be enhanced through the inclusion of the Bravais lattice. A Bravais lattice is an infinite array of discrete points which are generated by a set of discrete translation operators, and as a result, the Bravais lattice can be described by the vector equation as:

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3, \quad (2.1)$$

with $\vec{a}_i$ primitive vectors in the real lattice [77]. Miller indices are often used as a notation system in crystallography to indicate specific planes in Bravais lattices. Miller indices are indicated by (hkl) where h, k and l are integers and denote all planes which are orthogonal to the plane $h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$, where $\vec{b}_i$ are the basis of the reciprocal lattice vector $h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$, and where $\vec{b}_i$ are vectors in the reciprocal lattice (thus the Fourier transform of the Bravais lattice) [77,78]. Thus, Miller indexes of (111) and (001) in the xyz space indicates planes which are perpendicular to the vectors $\vec{r} = 1\hat{i} + 1\hat{j} + 1\hat{k} = \langle 1,1,1 \rangle$ and $\vec{r} = 0\hat{i} + 0\hat{j} + \hat{k} = \langle 0,0,1 \rangle$, respectively.

The principle functional in DFT approximations is the exchange-correlation functional. Among others, the Becke's hybrid exchange correlation description is a highly accurate method for describing the exchange-correlation behaviour of electrons in a complex system [4]. This method is, however, demanding in terms of computation time since the exact exchange-energy is calculated with the HTF-method, whereafter the calculated energy is mixed with the DFT-based exchange energy. The generalised gradient approximation (GGA) is computationally less demanding but provides less accurate adsorption energies [4]. As a result, uncertainties in E_{ad} calculated by using these methods cannot be smaller than ~ 0.25 eV, i.e. ~ 24 kJ·mol⁻¹ and therefore, the comparison with experimental studies is important. [4]. GGA are often more accurate than the local density approximation (LDA) since the change in electron density in the region around the point of interest are taken into account when GGA is used [4].

In solid-state reactions, the surface energy (γ) of a metal is defined as the free energy per unit area of a particular crystal facet: $\gamma = \frac{E_{free}}{A}$ [60]. Numerous processes, such as adsorption and crystal growth, depend on γ , which in turn determine the solid surface properties [60,79]. Consequently, γ may serve as a useful parameter to describe metal complex adsorption reaction systems [80]. Despite the practicality of γ , measuring the value of γ has, however, proven to be difficult [4].

2.13.3 Hybrid functionals and DFT

Large many-electron systems can be described more comprehensively, and with smaller errors, by using hybrid functionals [4]. Hybrid functionals combine HTF exchange with GGA where the general form of the hybrid functionals energy is described as:

$$E_{XC}^{hybr} = \alpha(E_X^{HF} - E_X^{GGA}) + E_{XC}^{GGA}, \quad (2.2)$$

with E_X^{HF} the Hartree-Fock exchange energy, E_X^{GGA} the GGA exchange energy, and α a semi-empirical exact-exchange mixing coefficient [66]. Various hybrid functionals have been developed, such as the Perdew-Burke-Erznherhof functional, which are often applied in molecular modelling.

2.13.4 The Perdew-Burke-Erznherhof functional

When the GGA is applied in solid-state chemistry, it is useful as a further refinement to include the Perdew-Burke-Erznherhof (PBE) exchange-correlation functional, i.e. GGA-PBE. In the PBE theory, the exchange-correlation energy (E_{XC}^{PBE}) of a multi electron system is calculated as:

$$E_{XC}^{PBE} = E_X^{PBE} + E_C^{PBE} = \int_0^r n \epsilon_X^{LDA} F_X^{PBE}(s) d\vec{r} + \int_0^r d\vec{r} n [\epsilon_{XC}^{LDA} + H_C^{PBE}(\vec{r}_s, \eta, t)]. \quad (2.3)$$

In this equation E_X^{PBE} and E_C^{PBE} are the exchange and correlation energies, respectively [66]. The PBE model also portrays a non-locality with the inclusion of an enhancement factor F_{XC} which leads to the exchange-correlation energy as [66]:

$$E_{XC}^{PBE} [n_\uparrow, n_\downarrow] = \int_0^r \epsilon_X^{unif}(n) F_{XC}(r_s, \zeta, s) d^3\vec{r}. \quad (2.4)$$

A further refinement is to include dispersion interactions and the subsequent Van der Waals energy. When dispersion interactions are taken into account the Van der Waals dispersion energy can be expressed as [81]:

$$E_{disp} = \frac{-1}{2} \sum_{i=1} \sum_{j=1} \sum_L \left(f_{d,6}(r_{ij}, L) \frac{c_{6,ij}}{r_{ij,L}^6} + f_{d,8}(r_{ij}, L) \frac{c_{8,ij}}{r_{ij,L}^8} \right), \quad (2.5)$$

with:

$$f_{d,n}(r_{ab}) = \left[1 + 6 \left(\frac{s_{r,n} R_0^{ab}}{r_{ab}} \right)^{a_n} \right]^{-1} \quad (2.6)$$

and

$$R_{0i,j} = \left(\frac{c_{8ij}}{c_{6ij}} \right)^{\frac{1}{2}}. \quad (2.7)$$

Herein $s_{r,n}$ is the order-dependent scaling factor for R_0^{ab} , R_0^{ab} is the cut-off radius, r_{ab} the radius between two system components and α_n the steepness parameter in the sequence equation $\alpha_{n+2} = \alpha_n + 2$ [81].

The function $f_{d,n}$ in eq 2.6, can be expanded by means of Becke-Johnson-damping (BJ). With the inclusion of BJ in DFT-D3, the functional $f_{d,n}$ subsequently changes to [82]:

$$f_{d,n}(r_{ab}) = s_{r,n} r_{ij}^n \left[r_{ij}^n + (a_1 R_{0ij} + a_2)^n \right]^{-1} \quad (2.8)$$

BJ often provides more accurate results for no-bonding interatomic distances in large systems and clearer effects of intermolecular dispersion are obtained [82]. As a result, the inclusion of BJ in DFT modelling of solid-state systems are often performed.

This damping accounts for the E_{disp} dispersion energy contribution from each closely spaced atom pair towards the total correlation energy [81]. In the equations above, N is the number of atoms, s_6 a density function-dependent global scaling factor, R_{AB}^n the interatomic distance between atoms A and B, and C_{6ij} is the dispersion coefficient of every atom pair AB in the system. It is important to note that this dispersion coefficient is geometry dependent since it depends on the relative distances between each atom pair and their surrounding atoms [81]. In addition, Becke-Johnson damping provides a clearer image of intramolecular dispersion in molecular structures [82].

The GGA approximation (model) of molecular systems can further be enhanced through the use of the conjugate gradient (CG) algorithm, which is a theoretical advancement on the steepest descent method [83]. In the CG algorithm, a new search vector is generated in each step based upon the current gradient, the gradient of the previous step, and the vector obtained in the previous step [84].

2.14 Molecular Modelling of adsorption on a metal surface

A simple, yet useful equation which can be used to simplify the total adsorption energy E_{ad} of a molecule X on a specific metal (M) surface in an isolated system, is:

$$E_{\text{ad}} = [E_{\text{MX}} - (E_{\text{M}} + E_{\text{X}})], \quad (2.9)$$

where E_{MX} is the energy of the adsorbed system, E_{M} the energy of the free M surface and E_{X} the energy of the free unadsorbed species (atom, ion or molecule) X [29]. Consequently, in this equation if $E_{\text{ad}} > 0$, adsorption of X to M will have a low probability of occurring and will not occur spontaneously since the energy of the adsorbed system is higher than that of the free species

and the pristine M surface. If $E_{ad} < 0$, adsorption will indeed occur to form a more stable adsorbed system. In general, it is preferable to express this equation in terms of the free-energy (G) that is: $G_{ad} = G_{MX} - (G_M + G_X)$. It is, however, important to keep in mind that E_{ad} is significantly affected by the orientation of the M and X in the case where X is not an atom but rather a multi atomic species such as an SO_2 molecule or a multi atomic ion, such as SO_4^{2-} .

As described in §2.13.4, the PBE functional provides a means to describe metal catalyst reactions in heterogeneous catalysis with considerable accuracy. As a result, the use of the GGA-PBE model serves as a viable choice to investigate the adsorption and oxidation of SO_2 on Pt(111).

In a similar manner, as used in the energy calculations of single-molecule adsorption systems, the energies of co-adsorption processes can be calculated as well. For the co-adsorption of two species X and Y on a metal surface M, the total adsorption energy of the system is calculated by:

$$E_{ad} = E(MX_{(ad)}Y_{(ad)}) - [E(M) + E(X_{(g)} + Y_{(g)})]. \quad (2.10)$$

Adsorption energy is an important quantity which can be used to describe the behaviour of adsorption. However, in addition to adsorption energy, the description of the adsorption process can be enhanced by the inclusion of other characteristics, such as the inclusion of charge distribution within a metal surface-adsorbate system.

2.15 Describing electronic behaviour of adsorption systems

In the kinetic theory of solids, Bader charge analysis (BC) provides a useful method to further evaluate the charge distribution and electronic properties of a solid-state system. Herein, the charge of every atom within an adsorption system is approximated individually.

Another influential factor on adsorption that can, serve as a useful parameter to describe the adsorption system, is the adsorption charge density (ρ_{ad}) as introduced in 2.13.1. Since the charge density of a metal surface is changed when adsorption occurs, ρ_{ad} can be expressed as the difference between the $\Delta\rho$ of the adsorbed MX system (ρ_{MX}) and the individual charge densities ρ_M and ρ_X of M and X:

$$\Delta\rho_{ad} = \rho_{MX} - (\rho_M + \rho_X), \quad (2.11)$$

respectively [29]. As a result, plotting the charge density as a function of reaction progress can aid in the determination of the reaction mechanism between M and X during the adsorption process [29].

One example wherein Δp_{ad} proves of significant use is in the visualisation of BC. Herein, Δp_{ad} of various species within the adsorption system can be calculated in order to describe the charge transfer behaviour between a metal surface and a specific adsorbate in full.

Both BC and Δp_{ad} can thus be employed to enhance the description of the adsorption as well as the oxidation behaviour of SO_2 on Pt surfaces, and can therefore aid in the identification of heterogeneous catalytic reaction mechanisms.

2.16 Conclusion

Although numerous experimental investigations regarding the adsorption and oxidation of SO_2 on Pt surfaces have been performed, very little mechanistic and computational research have been conducted. It has further been noted that various discrepancies still exist in literature over the mechanism and behaviour of SO_2 , both in terms of the adsorption process as well as its subsequent reactions with co-adsorbates, on Pt surfaces. Therefore, to address the shortcomings identified in this chapter, and to contribute to results from previous experimental and computational work discussed above, the co-adsorption behaviour of SO_2 and H_2O , as well as the adsorption of related sulphur oxides, on Pt surfaces needs to be investigated.

Pt serves as a highly efficient catalyst among various industrial processes. Pt has displayed substantial potential, in particular, as a catalyst for the HyS cycle. In this chapter, however, it was seen that poisoning of the Pt surface, as a result of SO_2 adsorption, is still, among others, a source of concern. In the following chapters, some of these uncertainties concerning the HyS cycle, are addressed.

CHAPTER 3 COMPUTATIONAL METHODS

3.1 Introduction

In this chapter, the computational modelling methods applied in this study are discussed. Firstly, details regarding the construction and characterisation of a pristine Pt(111) surface (§3.2 - 3.4) are discussed. Among the details is defining the specific calculation model and parameters used in the input files of the Vienna Ab-Initio Simulation package (VASP 5.4.1) [1]. Additionally, the optimal lattice parameters and vacuum spacing above the Pt(111) surface were determined.

It should be noted that in this chapter, some references to the following chapter (i.e. Chapter 4) are made, since some parameters within the methodology of the later analysis (e.g. adsorption energy determination) are dependent on the analyses results of systems that precede it (e.g. lattice parameters and vacuum spacing).

After the discussion of the specific methodology followed in the construction and characterisation of a pristine Pt(111) surface, the parameters for the modelling of single gas species are discussed in §3.5. In a similar manner to the pristine and single molecules discussions, the methods applied in the characterisation of SO₂ adsorption as well as co-adsorption systems are discussed (§3.4). Finally, the Bader Charge analyses methodology of the adsorbate systems are discussed in §3.5.

All the structures in this study were optimised, and properties, such as energy and charge distribution, were calculated using density functional theory (DFT). These DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP 5.4.1) and BIOVIA Materials Studio 2018 (18.1.0.2017) (DMol³ and CASTEP modules) software available at the Centre for High Performance Computing (CHPC) in Cape Town, South Africa [85–88]. Some structures illustrating the isosurface of charge transfer occurring on surfaces were constructed by using Visualization for Electronic and Structural Analysis (VESTA 3.5.3) software. The graphs and figures in this dissertation were created by utilising Origin Pro (2018 b9.5.1.195) and Inkscape (1.0.1) software, respectively [89,90].

The methodology followed in this study is summarised in the flow diagram presented in Figure 3.1:

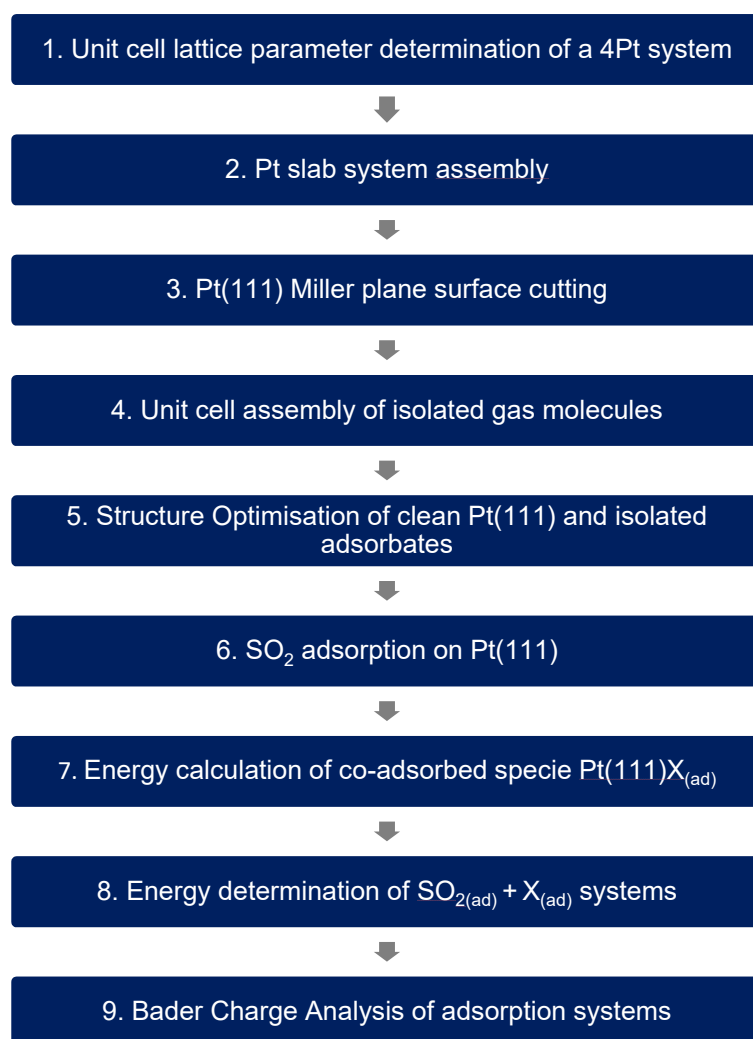


Figure 3.1: Flow diagram of the methodology followed in this study

3.2 Modelling of Pt bulk and the pristine Pt(111) surface

3.2.1 Calculation Model

A generalized gradient approximation with a Perdew-Burke-Ernzerhof exchange-correlation functional (GGA-PBE) with a projector augmented wave (PAW) method was used to optimise the Pt unit cell, bulk system, the Pt(111) surface and the single molecules [66,91–93]. All calculations were performed with spin-polarisation. GGA-PBE with Becke-Johnson damping and Van der Waals dispersion correction was applied [94]. All structures were geometrically optimised before energy calculations were performed. For the ionic relaxation of gas species as well as adsorption systems, a conjugate gradient (CG) algorithm was used, and for the electronic relaxation, a mixture of Davidson and RMM-DIIS algorithms were used [91,95]. For the optimisation, the evaluation of projection operators was configured to perform a fully automatic projection in real-

space. This was done in order to obtain more confined localised projector functions, whereas projections in single-point energy (SP) calculations were performed in reciprocal-space in order for the number of operators to be scaled with the number of plane-waves [87,96]. Dipole energy corrections were made for all systems wherein gas molecules were present, i.e. single gas species systems as well as adsorption systems, since these systems have a net dipole moment [88]. Although applying dipole corrections may slow convergence down, dipole corrections do correct leading force errors and enables the evaluation of asymmetric cells [97].

3.2.2 Vienna Ab-Initio Simulation Package (VASP 5.4.1)

In order to perform a calculation in VASP 5.4.1, four different files are needed to provide sufficient input [87]. Firstly, the coordinates of the various atoms in the system are defined in the POSCAR file [88,98]. Secondly, the KPOINTS file defines the required Blöch vectors that are used to sample the Brillouin zone [87,88,96]. The third file that is needed for any VASP calculation is the INCAR file. This file is used to define the specific calculation type and specific parameters, such as the electron count of systems consisting of charged species (for further detail see §3.2.2.1 below). The final file is the submission script file, wherein the hardware resources that are needed, the input files that should be used, the location where these files are, the output files (for example the CHGCAR and CONTCAR files) that are required, and finally where the output files should be copied to once the calculation is completed, are defined [88,99,100].

The CONTCAR file produced in a relaxation calculation contains the coordinates of all the atoms in the lowest energy arrangement identified in the calculation [88,99]. The CHGCAR file obtained from any VASP calculation contains the lattice vectors, the cell volume multiplied by the total charge density on the fine Fast Fourier transform grid (FFT-grid), as well as the PAW one-centre occupancies [88,100]. It should be noted that the CHGCAR file is not an explicitly user-defined input file, such as the INCAR and POSCAR files, but as mentioned in the previous paragraph, produced in a calculation [88,100]. Since the CHGCAR file does, however, contain significant information regarding the charge distribution within a system, it is of importance when Bader analysis is performed. In a case where the requested calculation time is too short, the CONTCAR could be copied as a new input of the atom coordinates (POSCAR values), whereafter the calculation could be repeated (see examples in **Appendix 6.3.1 and 6.3.2 p.139-140**). This iteration step could be repeated until a sufficient convergence value for the pristine Pt(111) is obtained.

Of all the files listed above the INCAR file is the most important, since it is the file wherein various parameters required for the calculation are specified. Therefore, the INCAR file will be discussed in more detail below. [88].

3.2.2.1 The INCAR-File

In this section, the parameters (both in terms of the specific mathematical models as well as the physical system relevant to any VASP calculation in this study) contained in the INCAR file are discussed individually.

The first parameter, namely the precision (PREC), is defined at the start of the INCAR file (see Appendix 6.4 - 6.5 p.141-143). This parameter defines the required accuracy of the calculation. As shown in Appendix 6.4 - 6.5 p.141-143, the precision (PREC) was set as accurate for all single-point energy calculations [88]. Furthermore, since the 5d⁹ electrons form the valence band of Pt, the mixing of band structures was set to calculate up to the d-band.

The next parameter (GGA) defines the type of generalised gradient approximation as the Perdew Burke Ernzerhoff (PBE) GGA (see §2.13.4 p.29) [66,87]. The non-spherical gradient correction contributions were included by activating the LASPH parameter (setting it to TRUE). In addition, the ISPIN parameter was set as 2, in order to perform spin polarised calculations for systems that contain gas molecules [88]. The performance of a spin polarised calculation is required since the spin interaction between the adsorbing molecule and the surface has a significant influence on the adsorption energy of the molecule [101]. In addition, the NUPDOWN parameter was not used since magnetic properties, i.e. the difference in the number of electrons with up-spin and down-spin, was not considered and since all ionic species contained paired electrons [88,102]. Since the band-structures were not calculated, the LDAU, LDAUTYPE, LDAUL, LDAUU and LDAUJ parameters were omitted [88,103–107].

For the Bader analysis, the magnetic moment parameter (MAGMOM), which specifies each atom's initial magnetic moment, was not activated since the CHGCAR file created by the relaxation and single point energy calculations already contains magnetisation densities [88].

With respect to hardware utilisation, four cores (NCORE) were used per atom orbital. Plane-wise data distribution in real space was not used and since KPAR, which determines the number of parallel treated k-points, was omitted, the four compute cores worked together on an individual k-point in a calculation [87,88]. The NBANDS parameter, which defines the number of bands, i.e. energy levels, within a calculation, was set as 8 x number of atomic cores in order to include a significant number of empty bands within each calculation [88,108].

The IVDW parameter that accounts for the additional distant-dependent intermolecular forces (dispersion forces) between the atoms and molecules in the adsorption systems, was set to a value of 12. This setting was done so that the DFT-D3 Van der Waals dispersion correction

method with Becke-Jonson damping, as described in §2.13.4, was invoked for both the optimisation and energy calculations of all the systems. [81,88,109]

For optimisation of the adsorption systems, the number of self-consistent electronic relaxation steps (NELM) used was 70, and for the ionic relaxation (NSW) 400 steps were performed, since it was expected that electronic relaxation convergence would be reached in fewer than 70 iterations. These numbers were chosen as such since the optimisation of the systems is normally achieved within these pre-set number of steps. However, the NELMIN parameter, which defines the minimum number of self-consistent field (SCF) minimisation steps, was not activated, since it is not required when the conjugate gradient algorithm is used in ionic relaxation, i.e. IBRION = 2 [88,95,110]. The IBRION parameter, which determines the update and movement of atoms, is kept constant within a specific calculation to use the conjugate gradient algorithm in finding the lowest energy structure in the optimisation of all the respective systems [88,95].

Regarding electronic relaxation criteria, a cut-off energy (ENCUT) of 400 eV was used with a default number of 70 electronic relaxation steps per calculation (defined by NELM) [88,111]. The ENCUT was selected so that it had a higher energy than the specified plane-wave cut-off energy of the augmentation charges in the pseudo-potential file (POTCAR) of the respective atomic species. The ENMAX energies, i.e. the maximum cut-off energy, in the POTCAR files of the respective atoms are 230.3 eV for Pt, 280.0 eV for S, 250.0 eV for H and 400.0 eV for O [111]. Thus, since O has the greatest EAUG value (400.0 eV), a cut-off energy of 400.0 eV will suffice. The termination criteria for convergence of electronic relaxation (EDIFF) was set to 10^{-4} eV and for ionic relaxation, a value (EDIFFG) of 10^{-2} eV·Å⁻¹ was selected [88,112,113]. The time-step (POTIM), which also serves as a scaling factor in optimisations, for the ionic motion was 0.1000 Å in both the relaxation and energy calculations [88,114]. The POTIM value was chosen to be rather small since a POTIM value which is too large might deliver too large relaxation steps, which, in turn, may cause a possible gap over the ideal minima [88]. Automatic optimisation of projection real-space operators (LREAL) was only performed for system optimisation [87,88].

Charge related parameters were only activated for charged systems. In these systems, the NELECT parameter was activated, and the total number of valence electrons in the system was indicated, e.g. in the SO⁺ cation NELECT would be 11 [88]. The NELECT parameter, however, was not activated for neutral species, since VASP automatically assumes that a given system is neutral, e.g. the NELECT parameter was omitted in neutral sulphur monoxide SO. In addition, the LMONO parameter was only activated for charged species to include monopole-monopole corrections in the calculation of the total system energy [87,88]. Furthermore, since no external electric force field was applied, the EFIELD parameter was omitted [115].

Different smearing settings were used depending on the specific system properties. However, the width of the smearing was kept constant to ensure that the difference between the free energy and the total energy (i.e. the term entropy $T \cdot S$) is negligible ($< 1.00 \text{ meV} \cdot \text{atom}^{-1}$). The optimisation of Pt(111) and the combined adsorption systems was performed by employing the first-order Methfessel-Paxton method (ISMEAR = 1), whereas Gauss smearing (ISMEAR = 0) was used in the optimisation of isolated gas species [72,87,88]. Gauss smearing was used as recommended for gas species and insulators by the VASP authors, whereas the Methfessel-Paxton method was specifically employed for Pt containing systems, in order to accommodate partial occupancies of orbitals [88]. In particular, during structural optimisation, a smearing width (SIGMA) of 0.05 eV was used, since this value is sufficient so that $T \cdot S < 1.00 \text{ meV} \cdot \text{atom}^{-1}$ [87,88,116]. Energy calculations of the optimised Pt(111) and optimised adsorption systems were performed with the Blöch corrected tetrahedron method by setting the ISEAMR value to -5 [74,87,88].

In terms of electronic properties, the parameter (LAECHG) for the writing of all the electron densities were activated for energy calculations to obtain the AECCAR0 file containing the core charge density, the AECCAR1 file containing the proto-atomic valence density and the AECCAR2 file which contains the self-consistent valence charge density [88,117]. The parameters for writing the local potential, electronic localised function, localised charges and localised orbital phase vectors were active in the energy calculations and written respectively as the LOCPOT (LVTOT parameter), ELFCAR (LELF parameter) and PROCAR (LORBIT parameter) files of the system [88,118–121]. Since the wave functions of the adsorption systems are unnecessary once the required output files have been obtained, the LWAVE parameter, which writes the individual wave functions of the solved Kohn-Sham equations to the WAVECAR file, was omitted [88,120,121]. In addition, although the local potentials (written to the LOCPOT file), the s-, p-, d- and site projected wave function character (written in the PROCAR file), and the electron localisation functions (ELFCAR file) are not required once a relaxation calculation is completed, the pbs script file was edited so that these files were removed at the end of a successful relaxation calculation, i.e. once convergence, as defined by the EDIFF and EDIFFG parameters, was reached.

Dipole corrections in the z-direction were applied for all systems that contained gas molecules by activation of the LDIPOL, which adds corrections to both the potential as well as the forces in VASP. Furthermore, LDIPOL adds monopole, dipole as well as quadrupole corrections in the energy determination, since the nearing of gas molecules to the surface were set in such a way that movement occurs only in the z-direction [97,122]. Note that the Pt(111)-vacuum interface lies in the xy-plane.

The evaluation of the partial band decomposed charge density (LPARD, EINT and NBMOD parameters) was not performed, and NMR shifts (activated by the LCHIMAG, DQ, ICHIBARE,

LNMR_SYM_RED and NLSLPLINE parameters in the INCAR file) were excluded since analyses of these characteristics are beyond the scope of this study [123–130].

3.3 Lattice Parameter

VASP software was utilised to construct a primitive cell containing a single Pt atom. A geometric optimisation of the primitive cell was performed with various lattice parameters (LP), whereafter a single-point energy determination was performed for each of the respective LP values. The calculated energies were plotted as a function of LP to obtain an energy minimum, of which the LP value ($x_{\min}$) corresponds to the optimal single-cell LP. Regression of the calculated energies as a function of LP had a minimum at an LP value of 3.9198 Å (see §4.2.1), which agrees well with experimental value of 3.9158 Å found in literature [131,132]. This parameter value is similar to the values obtained from previous studies [133–135]. The optimal single cell dimensions were further utilised to optimise the Pt primitive cell size and to assemble the four atom Pt unit cell [4]. The Pt unit cell was geometrically optimised. A Pt bulk system, consisting of 64 Pt atoms, was subsequently constructed by extending the dimensions of the unit cell two times along the x and y-axis in order to obtain the (2x2) cell.

3.4 Creating the Pt(111) and Pt Surface Stability

Pt(111) was created by cutting the relaxed four atom Pt unit cell along the (111) Miller plane. Metadise 5.64 was employed to cut the Pt bulk system and to obtain the required Pt(111) Miller index [136].

Within Metadise, the STACKGEN parameter (**Appendix 6.2 p.135**) was employed, wherein a systematic calculation was performed in order to identify symmetric surface slabs and where the Miller-plane should be cut (**Appendix 6.2 p.135**). In this case, the STACKGEN parameter was set to systematic, specifically in order to determine the mirror layers in the bulk structure (i.e. equivalent Pt layers in the bulk structure). Since the position of the first mirror layer was determined to be layer 1 (with layer 4 being the second mirror layer, i.e. ABCABC sequential order, see sum_o0001.out file in **Appendix 6.2 p.135**), the STACKGEN parameter was adjusted to 1, whereafter Metadise 5.64 was run once again in order to cut the 111 Miller surface, i.e. specifically on the first layer. In the input.txt file the precise ICSD (241737 for Pt), the atom charge (in this case 0), as well as the atomic mass of the atoms in the surface (i.e. 195.084u for Pt) were defined [87,137]. The output of the second run of the METADISE script would therefore contained the pristine Pt(111), which was used in all further analyses.

The Pt(111) used was symmetric, and additionally, the systems were kept non-polar to maintain the surface stability. Geometric optimisation was performed on the Pt(111), followed by system energy calculations. The energy determination of the unrelaxed system was performed by restricting the mobility of 32 Pt atoms into fixed positions in the slab without prior relaxation. In the surface energy calculations of relaxed pristine Pt(111), prior relaxation was performed. Some atoms were restricted in terms of mobility whereafter the energies were used to calculate the surface relaxation parameter of the 64 atom Pt(111) (§4.2.2) [138]. Furthermore, during the geometry optimisation of the pristine Pt(111) to obtain a relaxed surface, the top 32 Pt atoms of the surface were allowed to relax while the bottom 32 Pt atoms (unrelaxed) were constrained to stay in their initial positions.

Since a volume of space is required above the Pt(111) in order to investigate the adsorption of molecules onto the surface, the cell of the pristine Pt(111) system needed to be vertically elongated, i.e. a vacuum layer was added. As a result, vacuum layer thicknesses of 10.0 Å, 11.0 Å, 12.0 Å, 13.0 Å, 14.0 Å and 15.0 Å, respectively, were added above the Pt(111) before the surface optimisation. Thereafter, the total energies of the respective Pt(111) systems (differing only in terms of vacuum layer thickness) were calculated in order to determine the optimal vacuum layer thickness above the surface, i.e. the Pt(111) system with the vacuum layer thickness that corresponds with the lowest energy.

During geometry optimisation, as well as single-point energy determination, a 7x7x1 Monkhorst-Pack k-point mesh was used for both the pristine Pt(111), as well as for all of the respective adsorption systems [139,140]. Specifically, an uneven k-point mesh was used upon recommendation of the VASP authors [88]. The first-order Methfessel-Paxton smearing method (ISMEAR = 1) was employed for the structural optimisation of the Pt(111) and the combined Pt(111)-adsorbate systems, which were followed by energy calculations with the Blöch tetrahedron smearing method (ISMEAR = -5) [72–74]. The characterisation of Pt(111) was performed by optimisation of Pt(111) with a 14.0 Å vacuum layer, whereafter the surface energy of the pristine Pt(111) was calculated.

By using the surface energy of the unrelaxed and relaxed surfaces, the surface stability was determined with equations 3.1 - 3.3 [141]:

$$\gamma_u = \frac{E_{slab,u} - NE_{bulk}}{2A} \quad 3.1$$

$$\gamma_r = \frac{E_{slab,r} - E_{bulk}}{A} - \gamma_u. \quad 3.2$$

The percentage relaxation of the Pt surface was then calculated by:

$$\% \text{ Relaxation} = \left(\frac{\gamma_u - \gamma_r}{\gamma_u} \right) \cdot 100. \quad 3.3$$

In equations 3.1 - 3.3 $E_{slab,r}$ is the energy of the relaxed slab system, $E_{slab,u}$ the energy of the unrelaxed slab system, A the surface area and, γ_u and γ_r is the surface energy of the unrelaxed and relaxed systems, respectively. E_{bulk} is the energy of the 4Pt unit cell and $N = 2$.

3.5 Modelling of gas molecules

The free gas molecules investigated in this study were H_2O , SO_2 , SO_3 , O_2 , H_2SO_4 , HSO_4^- , H_2SO_3 , H_3O^+ , HSO_3^- , SO_4^{2-} and SO_3^{2-} . These species were optimised in a similar way to that of Pt(111). Some differences in parameters of the single molecule systems in comparison to Pt(111) will be discussed.

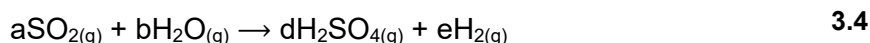
3.5.1 Calculation Model

Similar to the Pt surface stability calculations in §3.4, a GGA-PBE functional with PAW was used for the optimisation and SP calculations of the single adsorbate species [66,87]. A plane-wave cut-off energy (E_{cutoff}) of 400 eV and an 11 Å x 12 Å x 13 Å unit cell were used for each of the adsorbate species [66,87]. In the optimisation, as well as the SP energy determination of gas species, Gaussian smearing was applied. In the energy calculations of the various single gas-phase species, Gaussian smearing was employed again, and all calculations were spin polarised. In addition, a 1x1x1 k-point mesh was used for each of the isolated gas molecules.

3.5.2 Gas Molecules

An optimisation was performed for each free gas phase molecule to obtain the lowest energy molecular configuration, i.e. the ground-state structure. SP calculations were performed by using the optimised atomic positions for all the free gas phase molecules (H_2 , SO_2 , O_2 , H_2O , H_2SO_4 , H_2SO_3 , HSO_4^- , SO_4^{2-} , H_3O^+) before adsorption onto the pristine Pt(111) was performed [66,87].

The oxidation energy of SO_2 in the gas phase, i.e.



was calculated with:

$$E_{OX(g)} = \left[\frac{d}{a} E(H_2SO_{4(g)}) \right] + \left[\frac{e}{a} E(H_{2(g)}) \right] - [E(SO_{x(g)}) + \frac{b}{a} E(H_2O_{(g)})]. \quad 3.5$$

In equations 3.4 - 3.5, a , b , c , d and e are the stoichiometric coefficients, with $a = 1$, $b = 2$, $d = 1$ and $e = 1$.

3.6 Adsorption, Sequential Co-adsorption and Oxidation of SO₂ on Pt(111)

In order to obtain a comprehensive description of the electronic interaction between Pt(111) and the various adsorbates, energy determination, as well as Bader charge analysis, were performed. Different structural parameters of adsorbed molecules on the Pt(111), the influence of co-adsorption on energy determination, as well as the methodology for the determination of oxidation energies, are discussed.

3.6.1 Surface Adsorption, Relaxation and energy determination of adsorbed systems

After the optimisation of the Pt(111) with an optimum vacuum layer thickness of 14.0 Å (as will be discussed in Chapter 4) and the optimisation of the isolated gas phase species (molecules), e.g. SO₂, the gas-phase species were adsorbed in different geometries (i.e. sites and adsorption mode combinations) (Figure 3.2a-c) on the Pt(111) in order to simulate the adsorption process. Thereafter, the corresponding adsorption energies (E_{ads}) of SO₂, H₂O and related sulphur oxides were calculated.

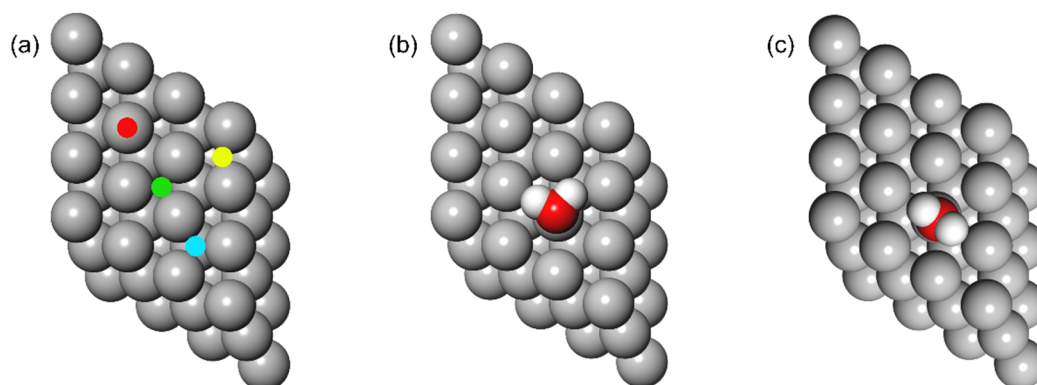


Figure 3.2: (a) Adsorption sites on Pt(111) (FCC=green; atop=red; HCP=cyan; bridge=yellow); (b) Parallel lying H₂O; (c) Perpendicular standing H₂O

Two adsorption orientations (angle limits) were found for planar triatomic molecules, such as SO₂ and H₂O, i.e. parallel and perpendicular (Figure 3.2b,c). It is important to note that only the two adsorption angle limits (for H₂O the angle between the horizontal plane i.e. the Pt surface and the H-O-H-plane, and for SO₂ the angle between the horizontal plane and the O-S-O-plane), i.e. parallel (0°) and perpendicular (90°) are illustrated in Figure 3.2. However, there are many adsorption angles between these two adsorption geometries with different energies, which may be characteristic of some adsorption systems. Consequently, for any chosen adsorbate, it is necessary that favoured adsorption sites (Figure 3.2a), as well as the most stable adsorption geometries, are identified. Pt(111) has three different general adsorption sites, namely atop (red

dot in Figure 3.2a), bridged (yellow dot in Figure 3.2a) and hollow sites. Hollow adsorption sites are further classified as FCC-hollow (green dot in Figure 3.2a) or HCP-hollow (cyan-dot in Figure 3.2a). In addition, adsorption modes for the different sulphur oxides, such as SO₂ and SO, are parallel, co-planar, S_b-bridged, O-bonded, O,O-bonded and S_a,O_a-bonded etc. These adsorption modes are presented and discussed in Chapter 4.

All the systems (i.e. pristine Pt(111) and single-molecule systems) were optimised before energy calculations were performed. After geometry optimisation, single-point energy calculations of the pristine Pt(111) and single molecules were performed. Thereafter, each adsorbate molecule was adsorbed individually onto the pristine Pt(111), in different geometries, to obtain unique adsorption systems. Each of the identified adsorption systems were geometrically optimised, followed by single-point energy calculations. In all structure relaxations and energy determinations the GGA-PBE model was employed.

A 7 x 7 x 1 Monkhorst-Pack k-point mesh was used for the adsorption calculations of the different Pt-adsorbate systems [139]. In addition, the convergence stopping criteria for structure optimisations were respectively set to 10⁻³ eV·Å⁻¹ and 10⁻⁵ eV, for ionic and electronic relaxation, with an accompanied smearing width of 0.05 eV. In addition, both the core and valence charge analyses of all systems, i.e. pristine Pt(111), gas-species and adsorption systems, were performed.

The obtained energies of the various SO₂ adsorption geometries were compared to evaluate the preference of SO₂ towards any particular adsorption geometry (site and adsorption angle), i.e. the lowest energy system. The adsorption energy of a molecule X was calculated by using equation 3.6.

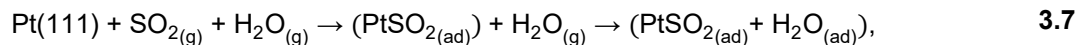
$$E_{\text{ads}} = E(\text{PtX}_{(\text{ad})}) - [E(\text{Pt}_{(\text{s})}) - E(\text{X}_{(\text{g})})] \quad 3.6$$

In the above equation $E(\text{PtX}_{(\text{ad})})$ is the energy of the combined adsorption systems, $E(\text{Pt}_{(\text{s})})$ the surface energy of the pristine Pt surface and $E(\text{X}_{(\text{g})})$ the free-energy of the gas phase molecule, respectively. The first-order Methfessel-Paxton smearing method (ISMEAR=1) was employed in the relaxation of adsorption systems followed by energy calculations with Blöch smearing in the tetrahedron method [72]. Thereafter, the Blöch tetrahedron method, as briefly described in Chapter 2, for single-point energy calculations of adsorption systems was employed [87, 142, 143].

The adsorption energies of other SO₂ related compounds on the Pt(111) surface were calculated. In addition, from the obtained energies of SO_{2(ad)} and SO_{x(ad)} systems, the oxidation energy of SO₂ was calculated.

3.6.2 Sequential co-adsorption of SO₂ and H₂O

In the event of co-adsorption on Pt(111) it should be noted that the order whereupon different molecules are adsorbed on the surface needs to be taken into consideration. Thus, for the co-adsorption of two molecules, namely SO₂ and H₂O, on Pt(111), in particular, whereupon SO₂ is adsorbed before H₂O, i.e.



the total adsorption energy of both SO₂ and H₂O is:

$$E_{\text{adsTOT}} = [E(\text{PtSO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})})] - [E(\text{Pt}_{(\text{s})}) + E(\text{SO}_{2(\text{g})}) + E(\text{H}_2\text{O}_{(\text{g})})] \quad 3.8$$

and the adsorption energies of the two individual adsorption steps are:

$$E_{\text{ads}}(1) = [E(\text{PtSO}_{2(\text{ad})}) + E(\text{H}_2\text{O}_{(\text{g})})] - [E(\text{Pt}_{(\text{s})}) + E(\text{SO}_{2(\text{g})}) + E(\text{H}_2\text{O}_{(\text{g})})] \quad 3.9$$

and

$$E_{\text{ads}}(2) = [E(\text{PtSO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})})] - [E(\text{PtSO}_{2(\text{ad})}) + E(\text{H}_2\text{O}_{(\text{g})})], \quad 3.10$$

respectively.

3.6.3 SO₂ Oxidation with H₂O

The oxidation of adsorbed SO₂ on the Pt surfaces was modelled by determining the adsorption energies of other sulphur oxides SO_x on Pt(111) and comparing the values to that obtained for SO₂. The oxidation energy of SO₂ was subsequently determined as the energy difference between the oxidised SO_x and the sum of the SO₂ and O₂ adsorption systems.

Oxidation of the respective SO₂ adsorbate modes was performed indirectly by adsorbing other SO_x and by obtaining the oxidised adsorbate energies, whereafter the corresponding oxidation energies were calculated. The total energies of the different adsorption geometries were compared to investigate both the susceptibility and stability of the individual Pt-X_(ad) systems adsorbates towards further oxidation.

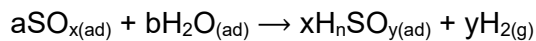
The tendency of the Pt surface atoms to be oxidised by the adsorbates was compared to the oxidation possibility of adsorbate molecules itself, serving as an indication of the corrosion effect that specific adsorbate species have on Pt surfaces. Lastly, the oxidation of the same adsorbate species, with different adsorption geometries, was modelled to evaluate the probabilities for the occurrence of the different Pt-surface-adsorbate interactions.

SO₂ oxidation was investigated both for oxidation of adsorbed SO_{2(ad)} on the Pt(111) surface as well as for the direct oxidation of SO_{2(ad)} by co-adsorbed H₂O. The formation of H₂SO₄, SO as well as other SO_x and H_ySO_x compounds were investigated. In addition, since higher sulphur oxides such as H₂SO₄ and H₂SO₃ are possible oxidation products of SO₂, the characterisation of adsorption systems that contain these species are required to evaluate the total oxidation energy of SO₂ on Pt(111). As such, the oxidation of adsorbed SO₂ on the Pt surfaces were modelled by using the energies of adsorbed and gaseous molecules e.g. for the oxidation reaction SO_{2(ad)} + H₂O_(g) → H₂SO_{3(ad)}, the oxidation energy was calculated as:

$$E_{\text{OX(ad)}} = E(\text{H}_2\text{SO}_{3(\text{ad})}) - [E(\text{SO}_{2(\text{ad})}) + E(\text{H}_2\text{O}_{(\text{g})})]. \quad 3.11$$

It is thus necessary that the energy of the adsorbed SO₂ system, as well as that of the adsorbed H₂SO₃ system, is known for the oxidation energy on the surface to be calculated.

Similar to the calculation of SO_x oxidation energies (E_{ox}) in the gas phase (equation 3.5), the oxidation energy of adsorbed SO_{2(ad)} on the pristine Pt(111), i.e. for the general reaction



was calculated according to equation 3.12.

$$E_{\text{OX(ad)}} = [E(x\text{PtH}_n\text{SO}_{y(\text{ad})}) + yE(\text{H}_{2(\text{g})})] - [E(\text{Pt}(a\text{SO}_{2(\text{ad})} + b\text{H}_2\text{O}_{(\text{ad})}))], \quad 3.1 \quad 3.12$$

In equation 3.12, a, b, x and y are stoichiometric coefficients and E(X) the energy of the respective gas species (X = SO₂, H₂O). Thus, since a = 1; b = 2; x = 1 and y = 1 in the HyS cycle, the oxidation energy will be:

$$E_{\text{OX(ad)}} = [E(\text{PtH}_n\text{SO}_{y(\text{ad})}) + E(\text{H}_{2(\text{g})})] - [E(\text{Pt}(\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}))]. \quad 3.2 \quad 3.13$$

3.7 Bader Charge Analysis

To investigate electron (e⁻) transfer during adsorption and oxidation, a Bader Charge (BC) analysis was performed. BC of pristine Pt(111), gaseous isolated species, as well as combined adsorption systems, were performed in order to identify which atoms are specifically involved in e⁻ transfer during adsorption and oxidation on the Pt surface [144,145].

BC analysis was performed, in VASP 5.4.1, with interactive bader and chgsum.pl scripts (see **Appendix 6.6 p.145**) to determine the BC of both Pt(111) and the respective adsorbates [87,145,146]. In the discussion in §3.2.2.1, it was noted that the calculated charges of any system

are written to the AECCAR0, AECCAR1, AECCAR2 and CHGCAR files. The AECCAR0 and AECCAR2 files, containing the core charge density and self-consistent valence charge density respectively, were summed by the chgsum.pl script in order to obtain the total charge of the system (CHGCAR_sum). Hereafter, the bader script was run using the system CHGCAR file and subtracting the CHGCAR_sum file as reference charge. BC analysis generates three files. The first file is the ACF.dat file containing the charge density maxima and the corresponding atomic volumes, and the second the AVF.dat file containing the volumes assigned to each individual atom in the system, specifically. The third file produced in a BC calculation is the BCF.dat file [147]. Although similar to the AVF.dat file, the BCF.dat file only contains the raw, unorganised output data of the Bader volumes. The ACF.dat file contains the single charge density maxima nearest to each atom in the system, thus avoiding noise from vacuum regions far from the atom centres. In this study, among the files produced by any Bader analysis calculation with VASP, only the ACF.dat file was used in the final evaluation of the charge transfer between the atoms. Therefore, charge-transfer between atoms can be identified through the charge analysis of equivalent atoms in different structures, e.g. the charge (obtained in the ACF.dat file) on the O atom of isolated H₂O with that of the O atom when adsorbed onto Pt(111). (Examples of the ACF.dat, BCF.dat and AVF.dat files are presented in **Appendix 6.6 p.145-143.**)

To illustrate the obtained BC of the respective adsorption systems three-dimensionally, iso-electron density surfaces were constructed with VESTA 3.5.3 [148]. To accompany the numerical BC values obtained with VASP 5.4.1, CHGCAR files of adsorption and gas systems were imported to VESTA so that the charge density differences could be visually presented. Herein, the electron density differences in atoms, between the gas and adsorbed phase, were illustrated through coloured iso-surfaces. Moreover, the precise location and structure of these surfaces can be modified to correspond to the ΔBC maxima in the spatial electron distribution in the system, i.e. the Bader surfaces.

3.8 Conclusion

In this chapter, the precise methodology followed in this study was coherently discussed. From the evaluation of various molecular modelling techniques discussed in Chapter 2, the model, in this case, DFT, as well as the accompanied parameters employed in this investigation, were discussed. In addition, the specific files of importance in performing DFT calculations with VASP were discussed as well as how the information contained within these files were evaluated. Furthermore, the analysis of selective data contained within these VASP files, such as the valence and core charge densities in the CHGCAR file, were discussed.

Specific parameters unique to every type of VASP calculation (i.e. optimisation, single-point energy determination and Bader analysis), as well as parameters that are common among different types of calculations (e.g. the specific functional employed), were discussed.

In the following chapters, the results obtained by applying the discussed methods are presented and discussed in order to develop a comprehensive understanding of the adsorption of SO_2 and other sulphur oxides (e.g. SO , SO_3), as well as the SO_2 - H_2O co-adsorption on $\text{Pt}(111)$, both in terms of reaction energy as well as charge-related properties.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the energy (E) and Bader charge (BC) analyses of the pristine Pt(111) surface, isolated single adsorbate molecules, and Pt(111) adsorbed molecule systems (single adsorbed and co-adsorbed) are presented and discussed. The calculated energies include Pt(111) surface energy, energies of isolated gas species (e.g. $\text{SO}_{2(g)}$), adsorption system energies, adsorption energies of single molecules (e.g. SO_2 adsorption on Pt(111)), as well as adsorption energies of co-adsorbed systems (e.g. SO_2 co-adsorbing with H_2O on Pt(111)). Comparisons between the co-adsorbate orientation and the BC properties are made to aid in identifying the preferred adsorption and oxidation mechanism of SO_2 on Pt surfaces.

In §4.2, the pristine Pt bulk and the Pt 111-Miller surface (Pt(111)) are presented. The surface parameters and results for the surface energy and BC analyses are presented and discussed. These results are subsequently compared to the structural properties of various $\text{PtX}_{(\text{ad})}$ systems.

Single-point energies (SP) for optimised isolated gas molecules/ions are presented in §4.3 and the reaction energies for gaseous species, in the absence of the Pt surface, were calculated in order to be compared with the corresponding reaction energies on the Pt surface.

The adsorption energy of various SO_2 adsorption geometries on Pt(111) are presented and discussed in §4.4. Herein, the most stable adsorption geometries were identified for further use in the evaluation of co-adsorption and SO_2 oxidation on Pt(111). Following the adsorption analyses of SO_2 , both oxidised and reduced SO_x and H_nSO_x ($x = 1 - 4$ and $n = 1 - 2$) species were adsorbed onto the Pt surface (§4.5 - §4.8). Thereafter, various pre-adsorbed and co-adsorbed species likely to be involved in the HyS process, were adsorbed on the Pt surface (§4.9) and characterised.

To further evaluate the interaction between co-adsorbed species, specifically between SO_2 and H_2O , as well as the energetic properties of H_nSO_x ($x = 1 - 2$ and $n = 3 - 4$) systems on Pt(111), energies of various $(n\text{SO}_2 + y\text{H}_2\text{O})$ co-adsorption systems (§4.10) were calculated. Energy determinations were performed both for the isolated gas molecules, as well as when adsorbed on Pt(111) to evaluate the reaction energies of 4.1 - 4.15 (p.60), respectively, and to determine the influence of a Pt catalyst on the reaction energies.

Following adsorption calculations of SO_2 , BC results of other oxidised sulphur species and co-adsorbed species are presented. This was to clarify further the probability of any electron transfer

that may occur between the Pt(111) and each of the respective adsorbate species X ($X = \text{SO}_2, \text{SO}_3, \text{H}_2\text{SO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{SO}_3, \text{HSO}_4^-$ and H_2O). In addition, BC analysis was employed to identify possible electron transfer between different co-adsorbed species. Finally, the oxidation energy, as well as the oxidation mechanism of adsorbed SO_2 on Pt(111), are discussed (§4.11.1 - §4.11.2). A systematic flow-diagram of this chapter is displayed in Figure 4.1.

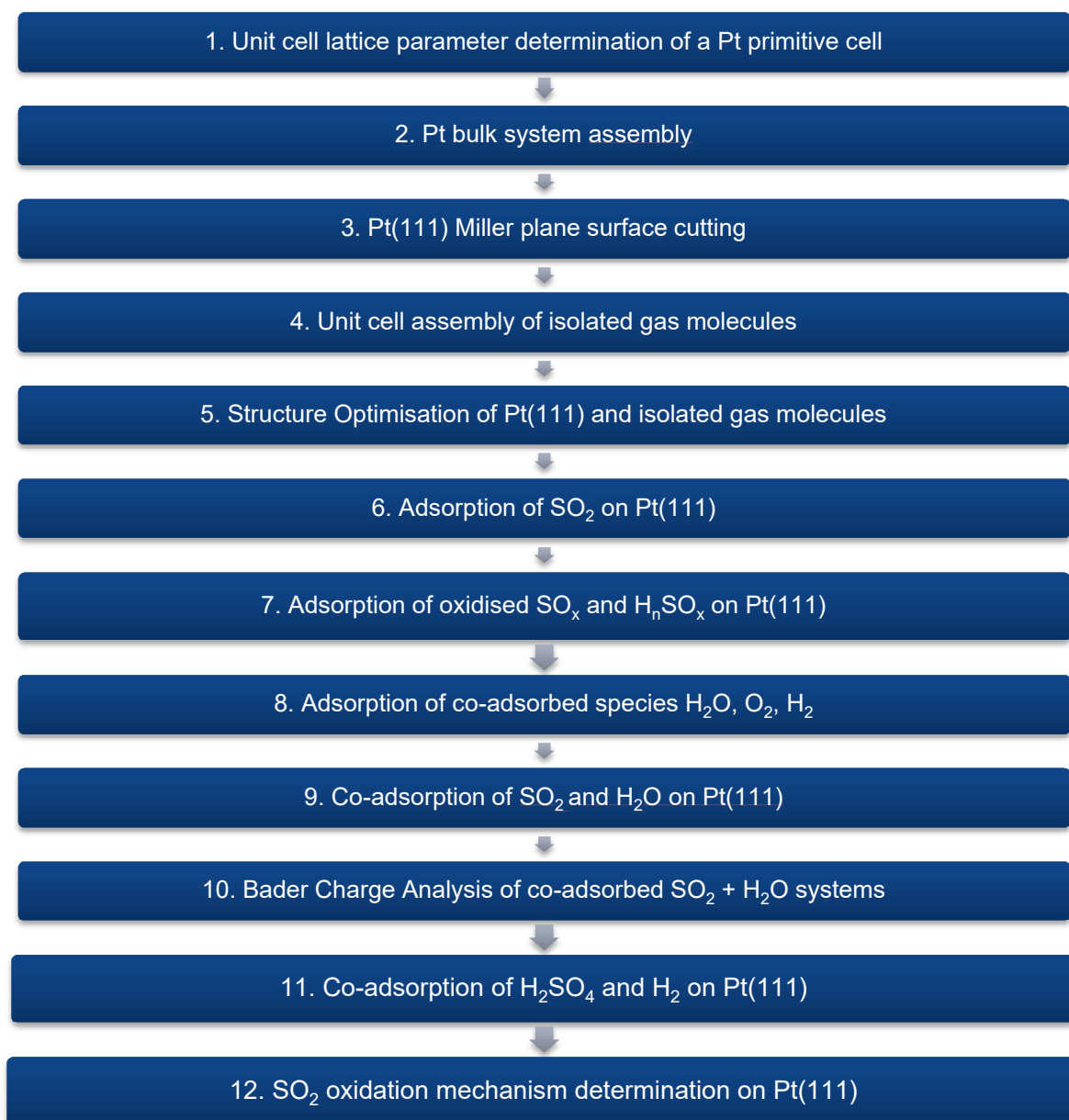


Figure 4.1: Outline of Chapter 4

4.2 Modelling of pristine Pt bulk and Pt(111) systems

The energy and structural results (lattice parameter results) for a unit cell containing a single Pt atom are discussed whereafter the surface energy and BC analyses results of the pristine Pt(111)

system (consisting of 64 Pt atoms) are presented and discussed (§4.2.1). Relaxation and energy results of the Pt(111) system with various vacuum distances are presented and discussed wherein the optimal vacuum spacing is identified (§4.2.2) in order to be used later for adsorption systems.

4.2.1 Pristine Pt bulk

Energy values and structural parameters of the optimised pristine Pt bulk are presented and discussed. The relaxation and lattice parameters, which were subsequently used to determine the optimal cell size for assembling of the Pt(111) system, are given as well.

Firstly, the energy of a primitive cell containing only one Pt atom was determined for different lattice factors. An optimised Pt unit cell containing four Pt atoms was analysed, for which an energy of $-6.860 \text{ eV}\cdot\text{atom}^{-1}$ was obtained. Results for the calculation of the adjusted lattice parameter are presented in Table 4.1 and Figure 4.2. Note that the adjusted lattice parameter (ALP) in Table 4.1 is calculated as the product of the lattice parameter (LP) and the lattice factor in order to identify the lowest energy geometry of the bulk Pt structure. It should be noted that the LP value of 3.854 Å , which is used as reference for the determination of the optimal lattice parameter for this study, was obtained from the ICSD FIZ Karlsruhe database [137].

Table 4.1: Energies of different unit cell lattice parameter (LP) values for a primitive cell containing a single Pt atom

<i>Lattice Factor</i>	<i>LP</i> (Å)	<i>ALP</i> (Å)	<i>E_{primitive cell}</i> (eV)	<i>E_{unit cell}</i> (eV)
0.95	3.854	3.661	-6.135	-24.539
0.96	3.854	3.700	-6.356	-25.422
0.97	3.854	3.738	-6.662	-26.649
0.98	3.854	3.777	-6.758	-27.032
0.99	3.854	3.816	-6.760	-27.039
1.00	3.854	3.854	-6.821	-27.284
1.01	3.854	3.893	-6.855	-27.420
1.02	3.854	3.931	-6.864	-27.455
1.03	3.854	3.970	-6.850	-27.401
1.04	3.854	4.008	-6.817	-27.268
1.05	3.854	4.047	-6.767	-27.067

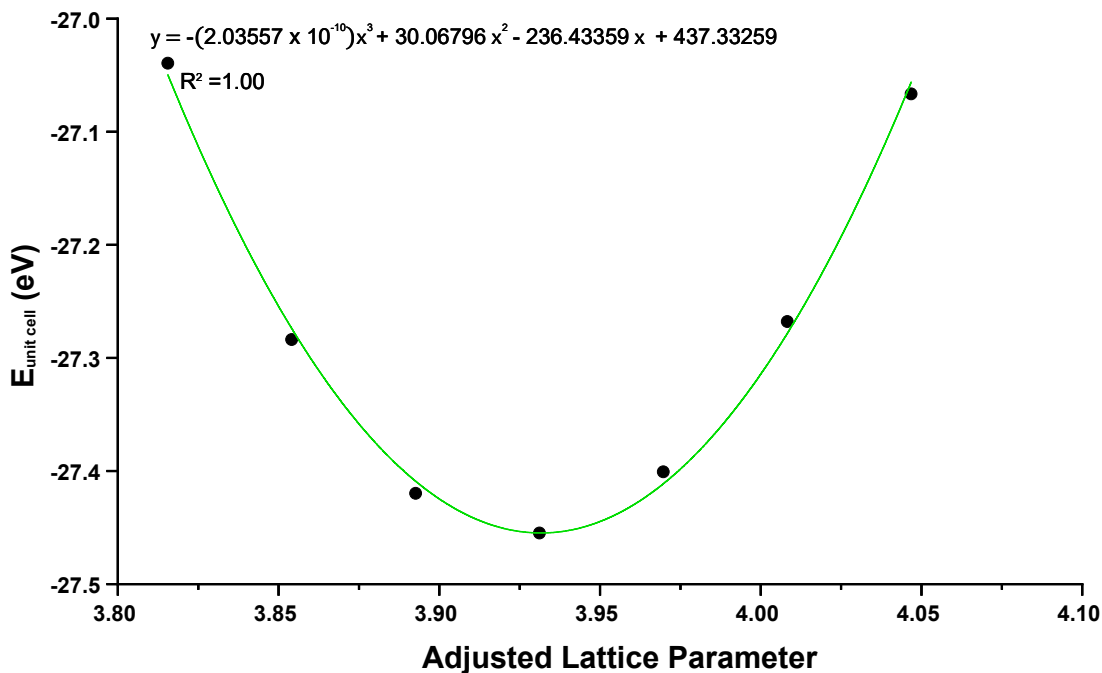


Figure 4.2: Energy profile of different lattice parameters for the determination of optimal cell dimensions.

In Table 4.1, it is observed that the optimal lattice parameter is between 3.90 Å and 3.95 Å. In order to identify the precise minima the derivative of the regression line in Figure 4.2 was determined. From the derivative, the optimal LP value of the Pt unit cell is 3.9189 Å (x-value corresponding to the energy minimum, i.e. $\frac{\partial E}{\partial LP} = 0$, in Figure 4.2) and correlates well with values found in the literature [13,133–135]. This value was subsequently used to calculate the required lattice dimensions of the Pt bulk system. The unit cell was increased to a p(3x3) Pt super cell with horizontal vector magnitudes of 11.089 Å and 9.602 Å. This Pt bulk system was cut along the (111) Miller plane to give the Pt(111) system.

4.2.2 Determination of vacuum spacing and energy of Pt(111) system

The geometrical parameters and structural properties of the Pt(111) system (i.e. a Pt slab created by cutting the Pt bulk along the 111-Miller plane) are presented and discussed. The energy as well as the electronic properties of the Pt(111) surface, are analysed and presented in order to be used as reference values for the investigation of the energies and electronic properties of adsorbed systems. However, before molecules can be adsorbed onto the surface an optimal vacuum spacing above the pristine Pt(111) surface is required to allow enough space for adsorbates, as well as to prevent both the interaction between surfaces and the interaction between an adsorbate and the repeating surface above the unit cell.

In order to determine the optimal vacuum spacing, the Pt(111) system energies with different vacuum spacings perpendicular to the surface, were calculated both for the relaxed and unrelaxed state of the system (Table 4.2) and illustrated in Figure 4.3.

Table 4.2: Energies for the pristine Pt(111) system with different vacuum spacings perpendicular to the surface

<i>Vacuum spacing</i> (Å)	<i>E</i> _{free-relaxed} (eV)	<i>E</i> _{free-unrelaxed} (eV)
10.0	-408.380	-408.316
11.0	-408.912	-408.287
12.0	-408.052	-408.268
13.0	-408.233	-408.253
14.0	-408.323	-408.245
15.0	-406.981	-406.905

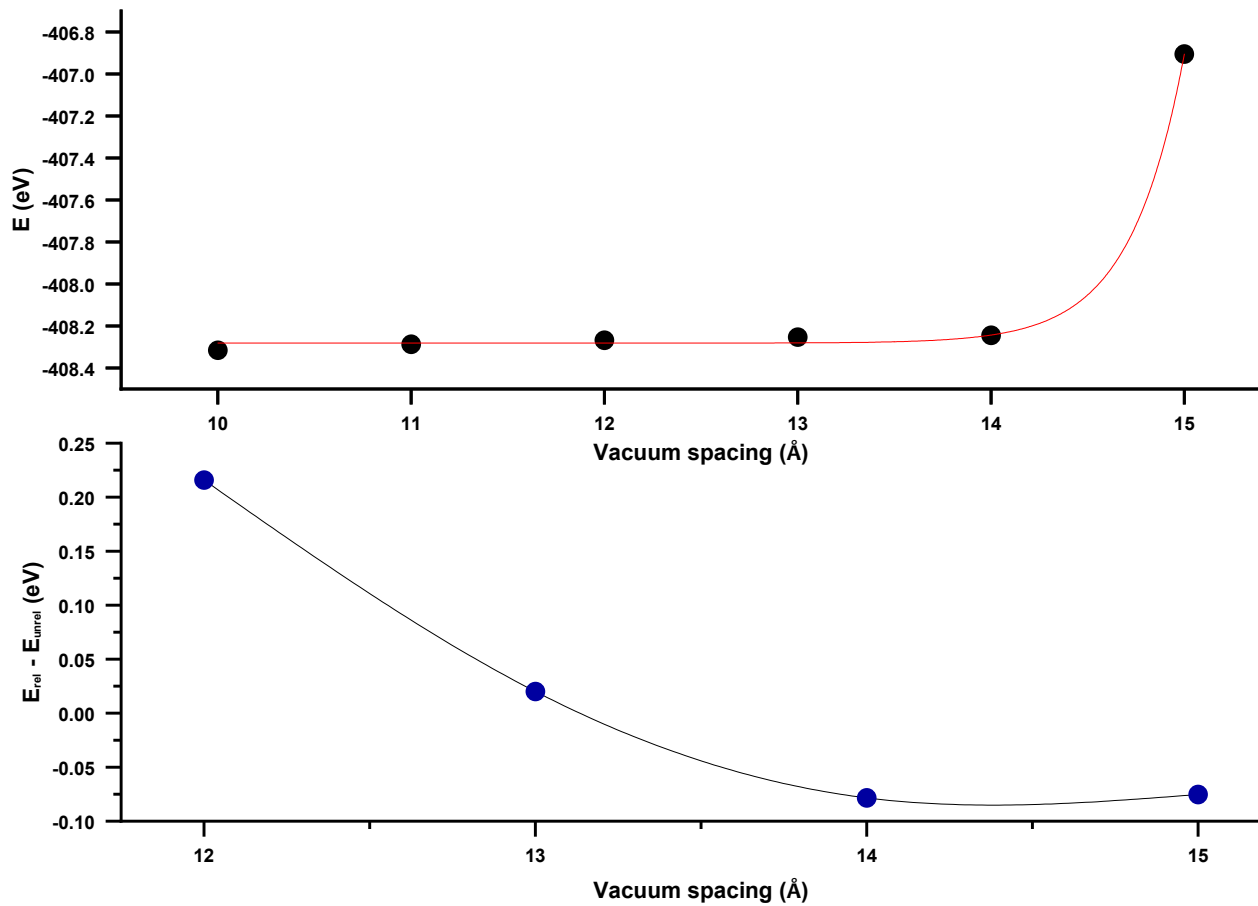


Figure 4.3: (a) Relaxed Pt(111) system energy and (b) Energy difference between relaxed and unrelaxed systems as a function of vacuum spacing.

From 10 Å to 14 Å in Figure 4.3a the energies of both the unrelaxed and relaxed surfaces are nearly constant with little variation around 408.27 eV. Upon reaching a vacuum distance of 15 Å (i.e. the distance whereupon an electron is removed from the surface) a significant increase in energy is observed. This increase is a result of a significant decrease in the interaction between

the surface and an electron. It is further noted that the energy difference between the relaxed and unrelaxed surfaces does not significantly change upon reaching a vacuum distance of 14 Å. Therefore from Figure 4.3 it can be concluded that the Fermi level of the surface is located at a distance between 14 Å and 15 Å from the top atom layer.

From the Pt(111) system energies, the optimal vacuum spacing above the surface was identified as 14.0 Å, since ($E_{\text{relaxed}} - E_{\text{unrelaxed}}$) starts to converge at this particular vacuum spacing, i.e. $E_{\text{relaxed}} - E_{\text{unrelaxed}}$ is sufficiently small (Figure 4.3a and b). All single molecule adsorption, as well as co-adsorption calculations (optimisation as well as energy determination), were subsequently performed with a 14.0 Å vacuum spacing.

The relaxed and unrelaxed free-surface energies subsequently used as reference energies in the calculation of the surface relaxation were $E_{\text{relaxed}} = -408.324$ eV and $E_{\text{unrelaxed}} = -408.245$ eV, respectively. From equations 3.1 - 3.3 (Chapter 3), dimensionless surface relaxation of the pristine Pt(111) is therefore 0.04%.

4.2.3 Structural properties of pristine Pt(111)

Since pristine Pt(111) is characterised by distinctive structural properties, such as its preference towards the FCC layer arrangement as well as having a specific geometry, the distances between adjacent Pt layers are measured in order to evaluate the influence of SO₂ adsorption on the Pt(111) structure.

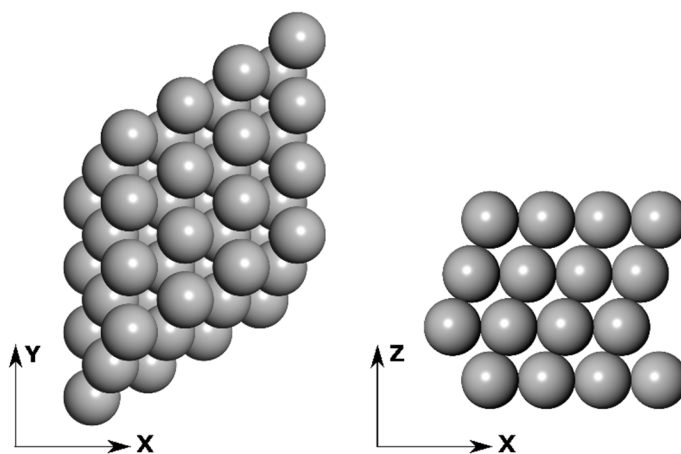


Figure 4.4: Top (left) and side (right) view of pristine Pt(111)

After optimisation, the average vertical spacing (z-direction) between two adjacent Pt layers i.e. between layers 1 and 2, layers 2 and 3 as well as layers 3 and 4, was 2.274 Å. An ABCABC layer arrangement, i.e. face-centred-cubic (FCC) was obtained for the Pt(111) system (Figure 4.4). The

nearest-neighbour-distance between two adjacent Pt in the Pt(111) was 2.803 Å, which corresponded well with the 2.80 Å obtained in the literature [149].

4.2.4 Bader Analysis for Pt(111) system

Bader charge (BC) analysis was performed for the pristine Pt(111) to aid in the analysis of the Bader results of the adsorbed systems PtX_(ad) that was investigated later in this study. The coordinates, as well as the corresponding BC of each Pt in the pristine Pt(111) system, are summarised in Table 4.3.

Table 4.3: Cartesian coordinates and Bader charges of Pt atoms in pristine Pt(111) consisting of 64 atoms

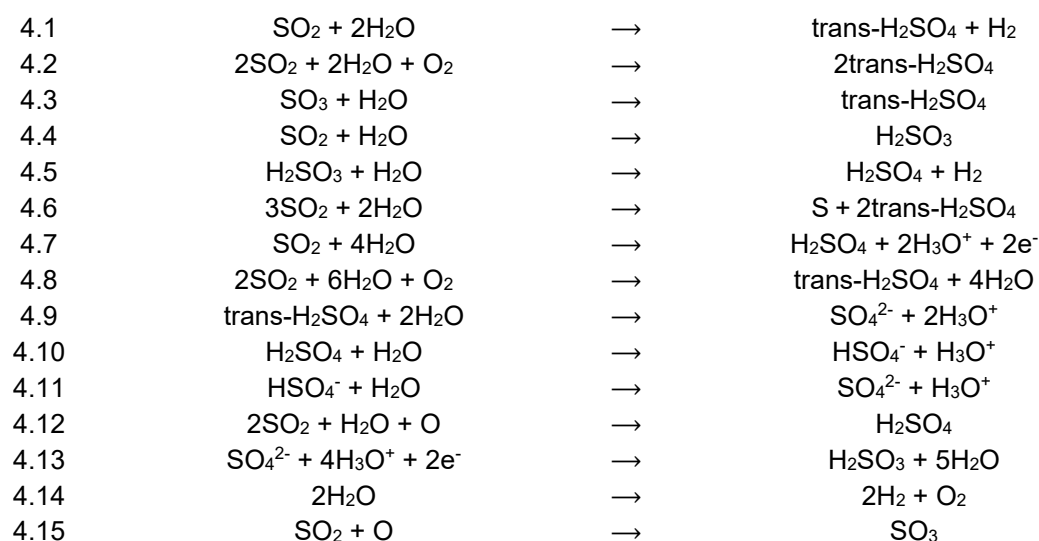
#	Coordinates			Charge	#	Coordinates			Charge
	X	Y	Z			X	Y	Z	
1	11.09	6.40	0.00	10.04	33	5.54	3.20	4.52	9.98
2	9.70	8.80	0.00	10.04	34	4.16	5.60	4.52	9.94
3	8.32	6.40	0.00	10.04	35	2.77	3.20	4.52	9.93
4	6.93	8.80	0.00	10.04	36	12.47	5.60	4.52	9.98
5	12.47	4.00	0.00	10.04	37	6.93	0.80	4.52	9.93
6	11.09	1.60	0.00	10.05	38	11.09	8.00	4.52	9.93
7	9.70	4.00	0.00	10.04	39	4.16	0.80	4.52	9.98
8	2.77	1.60	0.00	10.05	40	13.86	8.00	4.52	9.98
9	15.24	8.80	0.00	10.04	41	9.70	5.60	4.52	9.94
10	13.86	6.40	0.00	10.04	42	8.32	3.20	4.52	9.93
11	12.47	8.80	0.00	10.04	43	6.93	5.60	4.52	9.98
12	5.54	6.40	0.00	10.04	44	11.09	3.20	4.52	9.98
13	8.32	1.60	0.00	10.05	45	8.32	8.00	4.52	9.98
14	6.93	4.00	0.00	10.04	46	1.39	0.80	4.52	9.93
15	5.54	1.60	0.00	10.05	47	5.54	8.00	4.52	9.93
16	4.16	4.00	0.00	10.04	48	9.70	0.80	4.52	9.98
17	12.47	7.20	2.26	9.95	49	6.93	4.00	6.82	10.04
18	11.09	4.80	2.26	9.95	50	5.54	1.60	6.82	10.04
19	9.70	7.20	2.26	9.95	51	4.16	4.00	6.82	10.04
20	2.77	4.80	2.26	9.95	52	8.32	1.60	6.82	10.04
21	5.54	0.00	2.26	9.95	53	5.54	6.40	6.82	10.05
22	4.16	2.40	2.26	9.95	54	15.24	8.80	6.82	10.04
23	2.77	0.00	2.26	9.95	55	13.86	6.40	6.82	10.05
24	12.47	2.40	2.26	9.95	56	12.47	8.80	6.82	10.04
25	8.32	4.80	2.26	9.95	57	2.77	1.60	6.82	10.04
26	6.93	7.20	2.26	9.95	58	12.47	4.00	6.82	10.04
27	5.54	4.80	2.26	9.95	59	11.09	1.60	6.82	10.04
28	4.16	7.20	2.26	9.95	60	9.70	4.00	6.82	10.04
29	9.70	2.40	2.26	9.95	61	9.70	8.80	6.82	10.04
30	8.32	0.00	2.26	9.95	62	8.32	6.40	6.82	10.05
31	6.93	2.40	2.26	9.95	63	6.93	8.80	6.82	10.04
32	0.00	0.00	2.26	9.95	64	11.09	6.40	6.82	10.05
Total Bader Charge of pristine Pt(111)									640.0

The Bader charges of the pristine Pt(111) display a homogenous distribution of electrons, wherein each Pt atom is surrounded by ten valence electrons (Table 4.3). Note that although not every Pt atom has a valence electron count of precisely ten, the total valence electron count of the overall

system is indeed 640. The slight variation in the Bader Charge between identical Pt atoms can be ascribed to electronic effects. A slight variation in the charge distribution was observed from layer 1 to 2 and again from layer 3 to 4. Neighbour electronic repulsion gave rise to the observed charge distribution differences. Since layers 2 and 3 are situated between one atom layer above as well as another below, electronic repulsion by Pt atoms in these layers occurred upwards as well as downwards. In contrast, layers 1 and 4 are only neighboured by one layer each and therefore only experienced an electronic influence either from below (for layer 4) or above (for layer 1). As a result, layer 1 and layer 4 each experienced a unique electronic influence, through which their electron densities were affected differently. Since the electronegativity of all Pt atoms were identical, and the variation in BC for the Pt atoms in the Pt(111) system was small, it can be assumed that all of the Pt atoms are neutral and therefore do not have any net ionic charge.

4.3 Modelling of isolated adsorbates

In order to serve as a reference in the evaluation of the reactivity on Pt(111) surfaces in the oxidation of SO₂, the oxidation energies of the isolated gas species in the reactions related to the oxidation of SO₂ were calculated. Some of the proposed oxidation reactions (4.1 - 4.15) of SO_{2(g)} in the presence of O₂ and H₂O are listed below.[3,23]



The required reaction in the HyS cycle, to produce H₂, is shown reaction 4.1. Although some reactions do have a high probability of occurring, it should be noted, however, that the occurrence of some reactions, e.g. 4.9, has been opposed as well since SO₄²⁻ is adsorbed weakly on Pt [150].

Thus, single-molecule and ionic species were optimised, and energy calculations were performed (§4.3.1 and §4.3.2) in order to calculate the oxidation free-energies (ΔE_{free-ox}) of reactions

4.1 - 4.15 so that they can be used as reference in the interpretation of adsorption results later in this chapter.

In addition to the reactions above, two SO_2 molecules could react in a self-redox reaction to form SO_3 and SO , if reduction of SO_3 occurs the opposite of reaction 4.15 may occur. This reaction may be of interest in further investigations.

4.3.1 Isolated gas species (adsorbates)

Optimised structures of the aforementioned molecules, in reactions 4.1 - 4.15, are displayed in Figure 4.5.

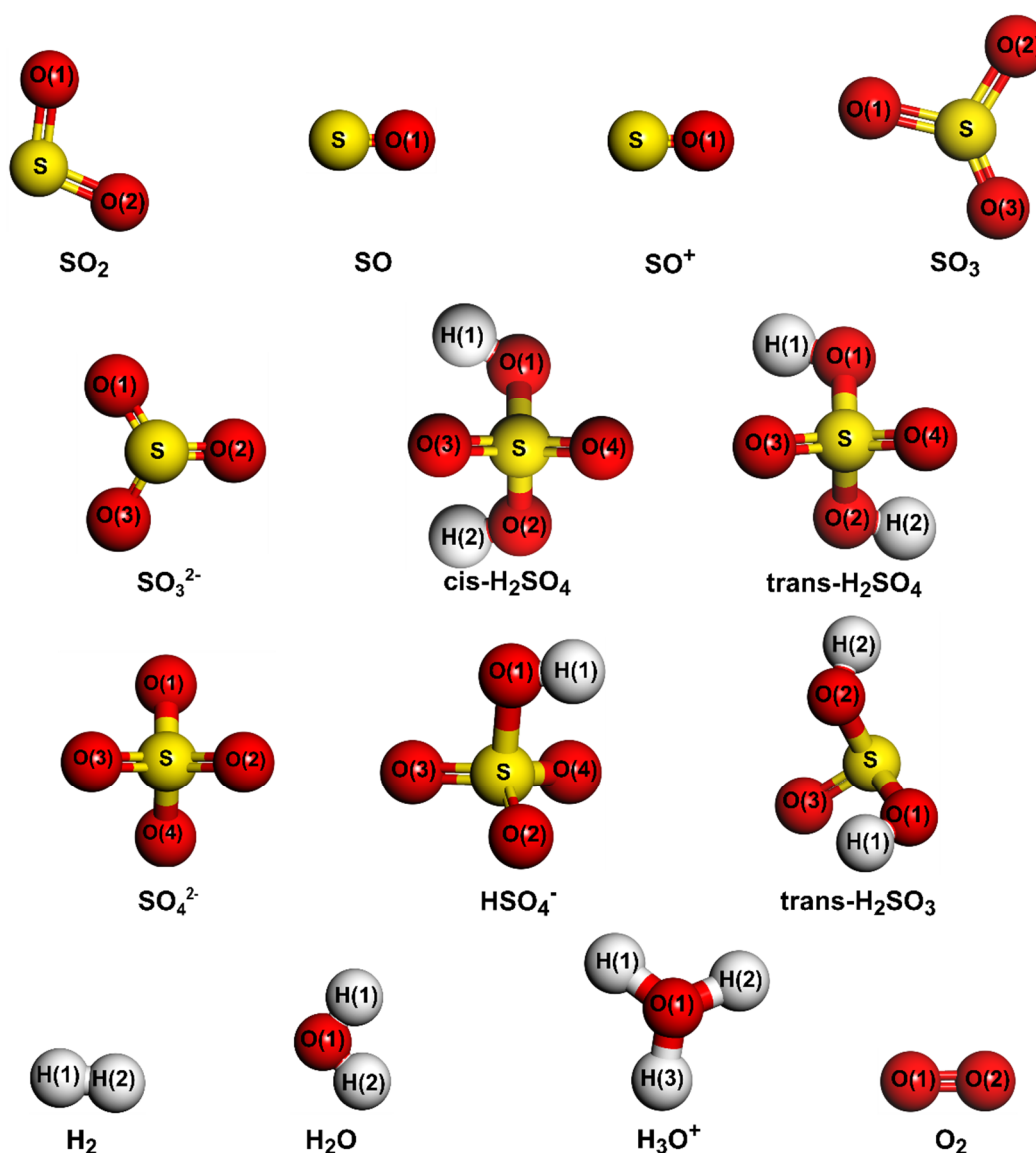


Figure 4.5: Molecular structures of gas species, SO_2 , SO , SO^+ , SO_3 , SO_3^{2-} , $\text{cis-H}_2\text{SO}_4$, $\text{trans-H}_2\text{SO}_4$, SO_4^{2-} , HSO_4^- , $\text{trans-H}_2\text{SO}_3$, H_2 , H_2O , H_3O^+ and O_2 . Standard colours are used throughout for hydrogen, oxygen and sulphur as white, red and yellow, respectively.

The structural properties (bond lengths and bond angles) of the free isolated gas species (molecules and ions) in Figure 4.5 are compared to the literature in Table 4.4(a and b) and Table 4.5 [135,151].

Table 4.4a: Calculated bond lengths (in Å) of isolated gaseous sulphur oxides (Literature values in parenthesis [135,152–154])

	SO ₂	SO	SO ⁺	SO ₃	SO ₃ ²⁻	SO ₄ ²⁻	trans-H ₂ SO ₄	cis-H ₂ SO ₄	H ₂ SO ₃	HSO ₄ ⁻
H(1)-O(1)							0.98 (0.98 ^a)	0.98 (0.98 ^a)	1.00	0.98
H(2)-O(2)							0.98 (0.98 ^a)	0.98 (0.98 ^a)	0.99	
H(2)-O(1)										
S-O(1)	1.43 (1.43)	1.50 (1.52 ^c)	1.43	1.43 (1.42 ^b ; 1.46 ^c)	1.50	1.51	1.61 (1.61 ^a ; 1.58 ^b)	1.61 (1.61 ^a)	1.60	1.70
S-O(2)	1.43 (1.43)			1.43 (1.42 ^b ; 1.46 ^c)	1.50	1.51	1.61 (1.58 ^b)	1.60 (1.61 ^a)	1.64	1.46
S-O(3)				1.43 (1.42 ^a ; 1.46 ^c)	1.50	1.51	1.43 (1.42 ^a ; 1.41 ^b)	1.44 (1.45 ^a)	1.45	1.46
S-O(4)						1.51	1.43 (1.44 ^a ; 1.42)	1.42 (1.45 ^a)		1.47

a: Ungerer et al. 2019 (GGA-PBE with double numerical plus polarisation); b: Demaison et al. 2007 (Møller-Plesset perturbation theory); c: Lin et al. 2004 (GGA-PW91)

Table 4.4b: Calculated bond lengths (in Å) of isolated gas species that may be co-adsorbed with SO₂ (Literature values in parenthesis [135,152–154])

	H ₂	H ₂ O	H ₃ O ⁺	O ₂
H(1)-O(1)		0.97 (0.97 ^a)	0.99 (0.97)	
H(2)-O(2)				
H(2)-O(1)		0.97 (0.97 ^a ; 0.97 ^b)		
O(1)-O(2)				1.24 (1.21 ^a)
H(2)-O(1)			0.99 (0.97)	
H(3)-O(1)			0.99 (0.97)	
H(1)-H(2)	0.75 (0.74)			

a: Jacob 2006 (GGA-B3LYP); b: Meng et al. 2004 (GGA-PW91)

Table 4.5: Calculated bond angles (in degrees °) of isolated (non-linear) gas species (Literature values in parenthesis [135,152,153,155])

	SO ₂	SO ₃	trans-H ₂ SO ₄	cis-H ₂ SO ₄	H ₂ SO ₃	HSO ₄ ⁻	H ₂ O	H ₃ O ⁺
O(1)-S-O(2)	119.4 (119.2)	120.0 (120.0)	102.3 (102.2)	101.1 (102.1 ^a ; 102.2 ^b)	97.16	104.5		
O(1)-S-O(3)		120.0 (120.0)	108.7 (108.5 ^a)	107.5	104.7	101.1		
O(2)-S-O(3)		120.0 (120.0)			104.5	115.4		
O(1)-S-O(4)			105.3 (105.7)	107.5		103.9		
O(2)-S-O(3)			105.4 (105.7)	109.4 (109.5 ^a)		115.4		
O(2)-S-O(4)			105.2 (105.7)	105.1 (105.8 ^a)		113.8		
O(3)-S-O(4)			124.4 (124.0)	123.9 (124.0 ^a)		115.7		
S-O(1)-H(1)			108.2 (108.5)	107.3 (107.0 ^a)	108.2	103.8		
S-O(2)-H(2)			108.2 (108.5)	108.9 (108.2 ^a , 108.6 ^b)	107.2			
H(1)-O-H(2)							104.5 (103.9 ^c ; 104.9 ^d)	112.7 (113.6)
H(1)-O-H(3)								112.7 (113.6)
H(2)-O-H(3)								112.7 (113.6)

a: Ungerer et al. 2019 (GGA-PBE with double numerical plus polarisation); b: Demaison et al. 2007 (Møller-Plesset perturbation theory); c Jacob. 2006 (GGA-B3LYP); d Meng et al. 2004 (GGA-PW91)

The bond lengths in SO₂ correspond well with literature values obtained by Meng et al., Jacob et al., Demaison et al. and Ungerer et al. ([135,152–154]). In general, the calculated bond lengths and bond angles of both H₂SO₄ isomers, correspond well with those found in the literature [152]. Slight deviations from literature values, e.g. the bond angle of SO₂, can be ascribed to small inherent uncertainties within DFT calculations as well as differences in functionals employed, i.e. PBE vs PW91 [66,156]. In addition, the bond lengths, as well as the bond angles of co-adsorbed species (H₂O, O₂ and H₃O⁺), correspond well with values found in the literature. For instance, the bond angle of H₂O, differ between the PBE and PW91 functionals, and the Møller-Plesset value. The differences observed may be an inherent result of the differences in the functionals itself, e.g. PW91 may, in some instances, be responsible for over-binding [157]. Although slight differences in terms of structural properties do exist between the values obtained in this study and literature, the differences are negligibly small (< 0.8%).

The energies of optimised single isolated gas species (molecules and ions) displayed in Figure 4.5 are summarised in Table 4.6.

Table 4.6: Energies of optimised isolated gas species

Molecule/ion	E_{SP} (eV)	E_{lit} (eV) [152,158]
S	-1.046	-1.12
SO ₂	-16.967	
SO	-9.132	
SO ⁺	1.119	
SO ₃	-23.073	
SO ₄ ²⁻	-28.750	
SO ₃ ²⁻	-21.472	
trans-H ₂ SO ₄	-38.182	-30.36 ^a
cis-H ₂ SO ₄	-38.128	-30.35 ^a
HSO ₄ ⁻	-36.511	
HSO ₃ •	-26.525	
H ₂ SO ₃	-31.240	
H ₂ S	-9.357	
H ₂	-6.760	-6.81 ^b
H ₂ O	-14.218	-14.24 ^b
H ₃ O ⁺	-9.190	
OH ⁻	-9.673	
O ₂	-9.883	-9.88 ^b
O	-0.909	-1.58 ^b
O ⁻	-0.361	

•: radical; ^a: Ungerer et al. 2019 (DFT modelled); ^b: Kattel et al. 2014 (DFT modelled)

Most of the gas molecules and ions in Table 4.6 do exist at $T = 0$ K, since $E_{free} < 0$. However, some species, such as SO⁺, are unstable and are highly unlikely to form as final oxidation products. These unstable species may form, either as short-lived intermediate oxidation products or as transition state species on pristine Pt(111). It should be noted that even though the energies of the gas molecules may differ from literature, the trend in their relative energies is similar. In addition, the phases i.e. gas, liquid or solid of the molecules that are observed will further influence their computed energies and as a result, the computed energies of this study may differ slightly from the experimentally obtained literature values. Furthermore, as seen in Chapters 2 and 3 the precise values of any DFT calculation will, inherently, always depend on the specific approximation, i.e. the generalised gradient (GGA) or the local density (LDA) employed as well as the specific functional e.g. GGA-PBE; GGA-PW91, LDA-PW92, being used [66,156]. For example, the energy of trans-H₂SO₄ was 0.054 eV lower than that of the cis isomer, a value similar to the 0.057 eV obtained by Ungerer et al. [152].

An important exception that should be considered in Table 4.6 is that of H₂. Inherently, DFT does not describe H₂ as accurately as it does with larger electronic systems since H₂, unlike other diatomic molecules, contains only two electrons [159]. Nevertheless, the energy of H₂ may still be used in adsorption analysis and compared to adsorption properties of other molecules such as

SO₂ since the difference between their energies is large enough to compensate for the overestimation of H_{2(g)}.

It should be noted that since the isomers of H₂SO₃ are highly unstable, and furthermore that, in general, trans-isomers have higher stabilities than the corresponding cis-isomers, only the trans-isomer is used in further analysis of SO₂ oxidation, both in the gas-phase, as well as when adsorbed on Pt(111) [160].

The values of the above-presented structural parameters, as well as the energies of the respective gas molecules, was compared later in this chapter, with that of the adsorbed molecules in order to identify specific structural changes that may occur upon adsorption.

4.3.2 SO₂ oxidation reaction energies in the gas phase

SO₂ oxidation energies were obtained for each of the respective reactions in 4.1 - 4.15, as well as those available in the literature, and the corresponding values, are summarised in Table 4.7.

Table 4.7: Gas-phase oxidation energies

	Reaction			ΔE_{free} (eV)	$\Delta H_{Lit.}$ (eV)
4.1	SO ₂ + 2H ₂ O	→	trans-H ₂ SO ₄ + H ₂	+0.461	+0.472 ^a
4.2	2SO ₂ + 2H ₂ O + O ₂	→	2trans-H ₂ SO ₄	-4.111	-3.341
4.3	SO ₃ + H ₂ O	→	trans-H ₂ SO ₄	-0.891	-1.073
4.4	SO ₂ + H ₂ O	→	H ₂ SO ₃	+11.237	
4.5	H ₂ SO ₃ + H ₂ O	→	H ₂ SO ₄ + H ₂	-10.775	
4.6	3SO ₂ + 2H ₂ O	→	S + 2trans-H ₂ SO ₄	+7.699	
4.7	SO ₂ + 4H ₂ O	→	H ₂ SO ₄ + 2H ₃ O ⁺ + 2e ⁻	+17.277	
4.8	2SO ₂ + 6H ₂ O + O ₂	→	trans-H ₂ SO ₄ + 4H ₂ O	-4.114	-3.341
4.9	trans-H ₂ SO ₄ + 2H ₂ O	→	SO ₄ ²⁻ + 2H ₃ O ⁺	+19.488	
4.10	H ₂ SO ₄ + H ₂ O	→	HSO ₄ ⁻ + H ₃ O ⁺	+6.703	
4.11	HSO ₄ ⁻ + H ₂ O	→	SO ₄ ²⁻ + H ₃ O ⁺	+12.785	
4.12	2SO ₂ + H ₂ O + O	→	H ₂ SO ₄	-5.820	
4.13	SO ₄ ²⁻ + 4H ₃ O ⁺ + 2e ⁻	→	H ₂ SO ₃ + 5H ₂ O	-25.538	
4.14	2H ₂ O	→	2H ₂ + O ₂	+5.035	+4.738
4.15	SO ₂ + O	→	SO ₃	-5.195	

- T is taken to be 0 K and therefore H = G; a: Shen et al. 2018 [161].

It should be noted that the precise energies of the reactions in Table 4.7 differ somewhat from literature. The reason for the observed differences is that, since only single molecular systems are investigated in this study, solvation effects were not taken into consideration. In real systems for reaction 4.1, for example, dissolved SO_{2(aq)} is surrounded by a large number of H₂O (i.e. the solvent) molecules, which increases hydrogen bonding, lowering the total energy. Some solvation effects, as well as subsequent energies of H₂SO₄ in an aqueous environment (i.e. multiple H₂O) have been previously described for this phenomenon [152]. However, since this study focused

only on the fundamental molecular behaviour on Pt(111), it is expected that differences in energies will be observed. Despite this, the tendencies of the reactions as observed in this study (i.e. whether ΔE_{free} is < 0 or > 0), did indeed correspond with literature.

In the gas phase, the formation of trans-H₂SO₄ via the reaction between SO₂ and H₂O is thermodynamically favourable (reactions 4.2, 4.8 and 4.12). However, reactions 4.1, 4.6 and 4.17, wherein H₂SO₄ is an oxidation product as well, do not occur spontaneously ($E_{\text{free}} > 0$).

Although the formation of SO₃ via the oxidation of SO₂ (reaction 4.15) is exothermic, it has been shown to occur rather slowly without a catalyst [162]. It is further noted that the formation of H₂SO₄ is thermodynamically favoured above the formation of H₂SO₃, not only for the reaction between SO₂ and H₂O (reaction 4.4), but also for various other possible substrate combinations (reactions 4.2, 4.3 and 4.8 (Table 4.7)). Thus, oxidation of SO₂ by H₂O and O₂ will occur readily leading to the formation of H₂SO₄.

Although H₂SO₃ is unstable under standard conditions ($T = 298.15 \text{ K}$; $p = 1 \text{ atm}$), i.e. it will undergo spontaneous decomposition to form SO₂ and H₂O, it may form electrochemically and in a strong cryogenic environment [3,160,163]. In contrast to H₂SO₄, H₂SO₃ is not always formed spontaneously and will thus (in the absence of Pt) be an unlikely reaction product. Furthermore, it is highly probable that the products in reactions 4.4 and 4.13 will react further to form lower-energy species.

The results above, regarding gas-phase reactions as well as that of the molecular structural properties, will be used further in this chapter as a reference in the analysis of the corresponding reactions on Pt(111). Possible intramolecular stereochemical changes in the adsorbing molecule, during the adsorption process as well as similarities and differences between gaseous and adsorbed-state oxidation of these species, was investigated.

4.4 SO₂ adsorption on Pt(111)

In this section, the adsorption energies of different SO₂ adsorption modes and sites, as illustrated in Figure 3.2, were calculated in addition to the characteristic properties, such as bond length and bond angles. The most favourable adsorption mode and site, i.e. geometry, as defined in Chapter 3, were identified and used in further calculations. Since the spacing between adjacent Pt(111) layers may change upon adsorption of the adsorbates depending on the strength of the Pt-adsorbate interaction, the structural properties of the Pt(111) in the adsorbed systems were investigated as well.

4.4.1 Adsorption energy and properties of SO₂

Various adsorption modes with a variety of binding sites are displayed in Figure 4.6, for which each corresponding adsorption energy was calculated. It should be noted that the adsorption geometry of SO₂ is defined both by its position (e.g. FCC, HCP, atop or bridged) and mode (e.g. S-bonded, O-bonded, S,O-bonded) on the surface, as well as by the adsorption angle between SO₂ and the Pt surface. The number of adsorbate atoms directly bonded to a surface Pt atom is indicated by η^x with x the number of atoms in the adsorbate bonded to at least one Pt atom, e.g. FCC- η^2 -S_b,O_a represents that S is adsorbed in a bridge site between two Pt atoms and O is positioned in an atop-site above a top-layer Pt atom.

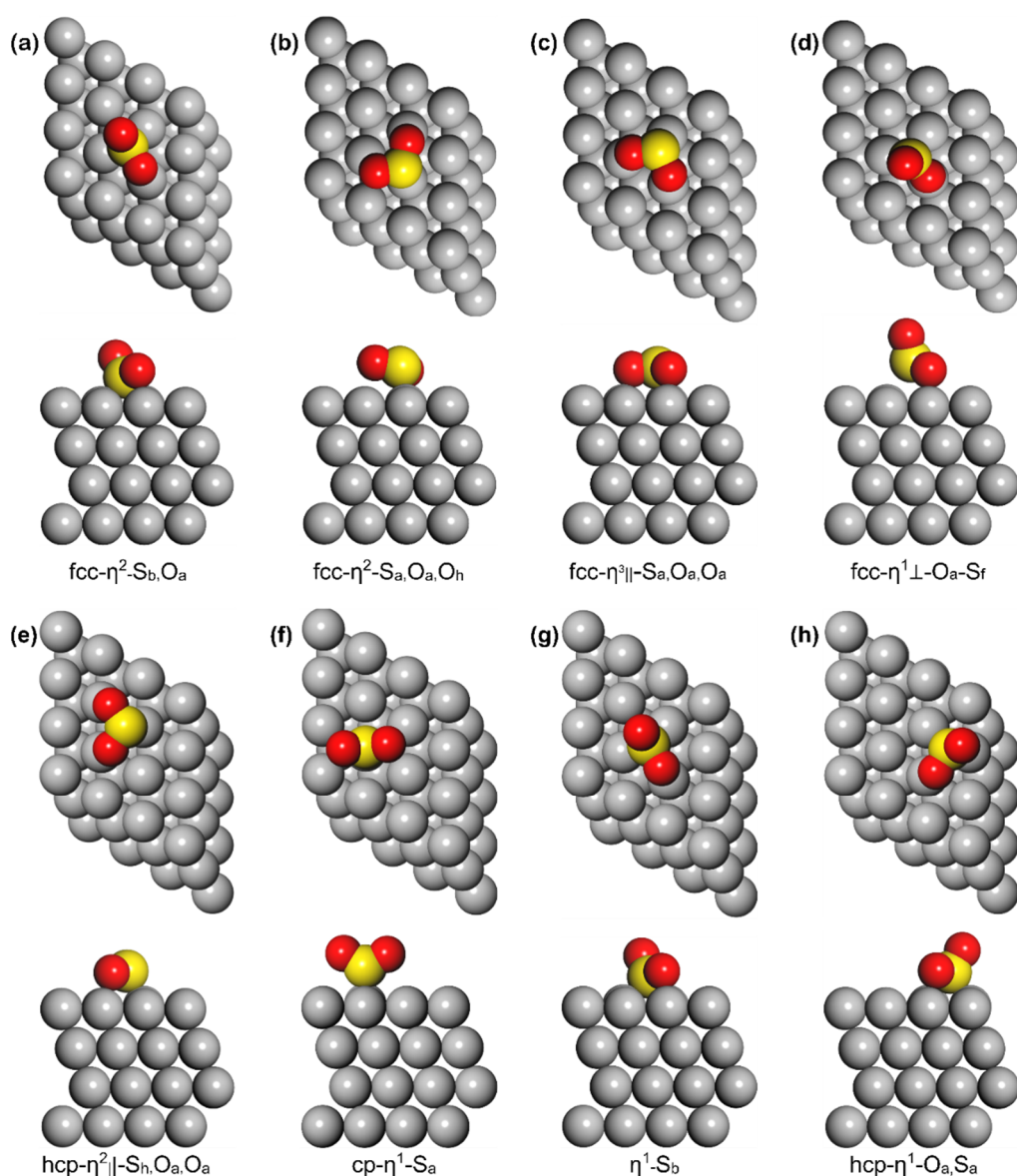


Figure 4.6: Top and side views of different SO₂ adsorption geometries on Pt(111)

The calculated SO₂ adsorption energies on Pt(111) (Figure 4.6) of the respective adsorption geometries, i.e. PtSO_{2(ad)} are summarised in Table 4.8 and compared in Figure 4.7. The

adsorption free-energy ($E_{\text{free-ads}}$) of each adsorption geometry was subsequently calculated according to equation 3.6, and the corresponding values are presented. The adsorption distances of each adsorption geometry display a significant variation (~ 0.42 Å difference) between the shortest and longest adsorption geometries. Note that in Table 4.8 the perpendicular adsorption distance, $d_{\text{adsz}\perp}$, is defined as the vertical distance i.e. z-direction distance, between the nearest top layer Pt ad the nearest atom of the adsorbed SO_2 .

Each of the adsorption geometries in Table 4.8 is characterised by a negative $E_{\text{free-ads}}$ value, indicating the formation of relatively stable $\text{SO}_{2(\text{ad})}$ adsorption systems in comparison to pristine Pt(111) and isolated gaseous SO_2 .

Table 4.8: Adsorption energies of some SO_2 adsorption geometries

Adsorption geometry	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	$d_{\text{adsz}\perp}$ (pm)	θ_{ads} (°) ^b	$E_{\text{ads-lit}}$ (eV) [6][6,13]	Figure 4.6
FCC- η^2 -S _b ,O _a	-427.043	-1.752	168.51	90.0	-1.85 ^c	(a)
FCC- η^2 -S _a ,O _a ,O _h	-426.640	-1.349	207.19	15.8		(b)
FCC- η^3 -S _a ,O _a ,O _a	-426.816	-1.524	207.45	0.0	-1.11 ^a	(c)
FCC- η^1 _⊥ -O _a -S _f	-425.928	-0.637	213.83	90.0		(d)
HCP- η^2 -S _h ,O _a ,O _a	-426.783	-1.492	210.07	0.0	-1.07 ^a	(e)
cp- η^1 -S _a	-426.464	-1.172	216.95	90.0		(f)
η^1 -S _b	-425.834	-0.542	167.96	90.0		(g)
HCP- η^1 -O _a ,S _a	-426.500	-1.208	210.49	67.6	-1.06	(h)

Subscripts, || = parallel; ⊥ = perpendicular; f = FCC-hollow; h =HCP-hollow; a = atop; b = bridged; cp = co-planar; η^n = n-bonded and FCC = face centered cubic; HCP hexagonal close-packed; ^bHappel et al. and ^aLin et al. [45] used the PW91 functional and not the PBE functional. ^bAdsorption angle measured relative to Pt(111) surface i.e. the xy-plane; ^cUngerer et al.

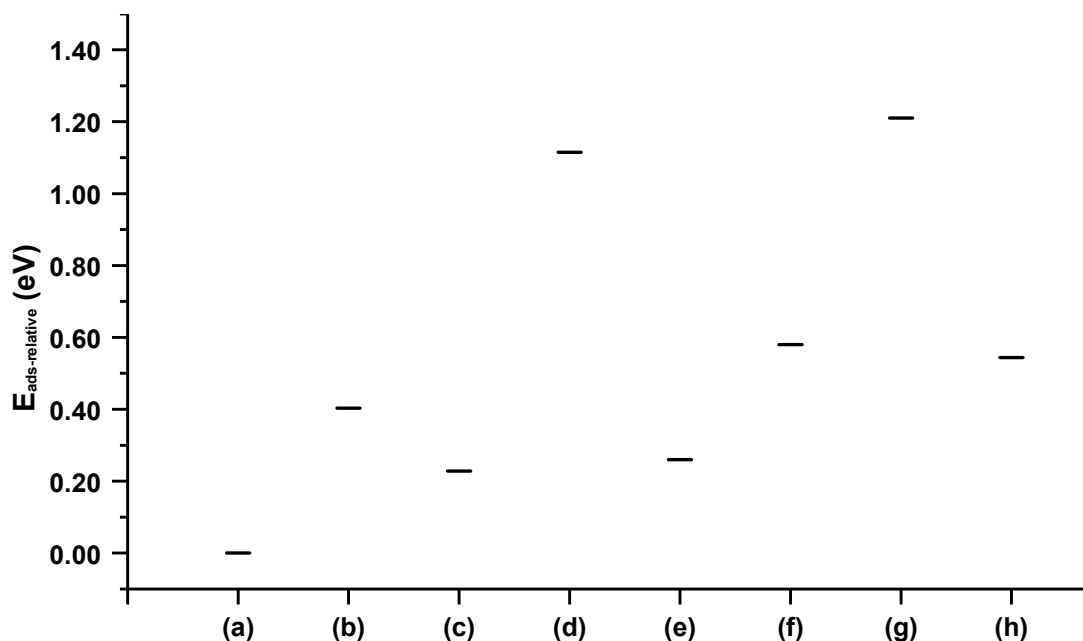


Figure 4.7: Adsorption energies of various SO₂ geometries relative to the strongest adsorption geometry i.e. Figure 4.6a

SO₂ is preferentially adsorbed in the η^2 -FCC-S_bO_a geometry (Figure 4.6a) on Pt(111) (see Table 4.8) having the greatest adsorption-free-energy ($E_{\text{free-ads}} = -1.752$ eV). The identification of FCC-S_bO_a as the most favourable adsorption geometry, is in agreement with previous studies concerning SO₂-adsorption on Pt(111) [6,13,28,45,152]. It is noteworthy that a strong adsorption preference towards this particular adsorption geometry exists (Figure 4.6a), it being significantly lower (~ 0.228 eV) in energy than Figure 4.6c. The geometries displayed in Figure 4.6c and Figure 4.6e have particularly similar adsorption energies. This may suggest that both geometries can co-exist in equal amounts when equilibrium is reached, furthermore, if the energy barrier between these two geometries is small enough, quick interchange between them (from statistical mechanics) given that the thermal energy of the system is sufficient. These two adsorption geometries may be regarded as having intermediately strong binding between the surface and the adsorbed SO₂.

Similarities in energy were also observed when Figure 4.6f and Figure 4.6h are compared. In Figure 4.6h, the SO₂ is adsorbed in the HCP position and is not perfectly perpendicularly adsorbed. However, in Figure 4.6f, SO₂ is indeed perpendicular to the surface but, in this case, the S is adsorbed in the atop position and not in the preferred bridged position. Since, at standard temperature (298.15 K) the thermal energy kT is ~ 26 meV, (with k the Boltzmann constant) and since both electrode reactions in the HyS cycle take place at temperatures > 323.15 K, the rest of the adsorption geometries, i.e. Figure 4.6b-h, may, however, convert via rotation of the SO₂ to the FCC-S_bO_a adsorption mode. Since the energy of the FCC-S_bO_a geometry was more than 0.18 eV

lower than that of the second most stable geometry, a significantly higher T is required to alter the adsorption geometry of FCC-S_b,O_a adsorbed SO₂.

A detailed view of the PtSO_{2(ad)} FCC-S_b,O_a geometry (most stable) is displayed in Figure 4.8.

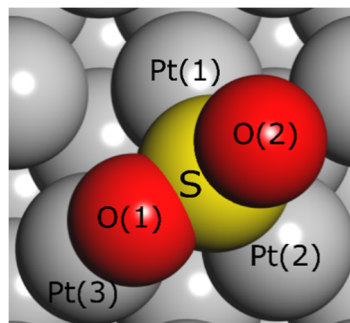


Figure 4.8: Top view of FCC-S_b,O_a adsorbed SO₂ on Pt(111)

Despite the apparent similarity of the adsorption geometries illustrated by Figure 4.6a, Figure 4.6d and Figure 4.6g, significant differences in their adsorption energies were observed. One notable structural difference between the geometries illustrated in Figure 4.6a,g is their adsorption angles (44.403° compared to 42.263° in Figure 4.6 a and g, respectively), which may well be the principle stereochemical factor influencing the difference between their adsorption energies. Since the energies of the geometries illustrated in Figure 4.6a,d,g differ substantially, despite their similarity in appearance, it may well be that the geometries illustrated in Figure 4.6d,g serve as intermediate products that form in the initial adsorption stages, which undergoes further rearrangement to subsequently form the geometry in Figure 4.6a as the final adsorption product. This intermediate formation is also possible for the geometries in Figure 4.6b and Figure 4.6c having adsorption energies differing significantly from one another. Another explanation for the small adsorption energy of the adsorption geometry in Figure 4.6g may be the adsorption distance. Although the adsorption distance of the geometry in Figure 4.6g is similar to that illustrated in Figure 4.6a, Coulomb repulsion may well be a contributing factor in the geometry displayed in Figure 4.6g, which subsequently weakens the adsorption energy.

The adsorption distances, bond lengths and angles of adsorbed SO₂ in the η²-FCC-S_b,O_a geometry, as illustrated in Figure 4.8, in comparison to the free isolated SO₂ molecule, are summarised in Table 4.9. The positional displacement of the three directly bound Pt(111) top layer atoms from their original positions are presented as well.

Table 4.9: Comparison of the structural properties of isolated and adsorbed SO₂ and three directly bonded Pt atoms

Property	Isolated SO _{2(g)}	Adsorbed FCC-S _b O _a SO _{2(ad)}	Positional displacement of Pt atom during adsorption (Å)
r[S _b -O _a (1)] (Å)	1.428	1.450 (1.46 ^b)	-
r[S _b -O(2)] (Å)	1.428	1.514 (1.53 ^b)	-
θ[O _a (1)-S _b -O(2)] (°)	119.4	114.5 (114 ^b)	-
r[S _b -Pt(1)] (Å)	-	2.276 (2.31 ^a)	0.162
r[S _b -Pt(2)] (Å)	-	2.254 (2.31 ^a)	0.136
r[O _a (1)-Pt(3)] (Å)	-	2.298 (2.30 ^a)	0.039

*O¹ is bonded to the Pt (Literature values in parenthesis [6,13,45,164])

^a Lin et al. 2002; ^b Happel et al. 2011

The perpendicular adsorption distance of the SO₂ in Figure 4.8 is 1.77 Å, which corresponds well with the 1.73 Å obtained by Happel et al. [6]. Furthermore, stretching of both S-O bonds (in SO₂) occurred during adsorption with a ~0.032 Å increase in bond length between the S and the directly surface-bound O_a. A mean positional displacement of ~0.112 Å, towards the adsorbing SO₂, was observed for the three Pt atoms located nearest to SO₂ during adsorption. These structural changes were simultaneously accompanied by a decrease of ~6° in the O-S-O bond angle θ. The accompanied structural changes within SO₂ upon adsorption on Pt(111) are a direct result of the electronic interaction between the surface and the adsorbate. In particular, the Pt atoms which are bridged by the S, (Pt(1) and Pt(2)), underwent a relatively large displacement (~0.148 Å) in comparison to the O-bonded Pt(3) (~0.039 Å). These changes in internal bond lengths and bond angles are a result of the electronic interaction between Pt and SO₂, and will influence the reactivity of both Pt and SO₂ towards other co-adsorbed species, such as H₂O. Consequently, as a result of these structural changes, the energy of the reactions between adsorbed SO₂ and other co-adsorbates (such as H₂O), may differ from the energy in the gas phase. These results, regarding the structure of adsorbed SO₂, are in accordance with observations made in previous studies regarding bond lengths, bond angles and adsorption distances [6,45]. In addition, the spacing between adjacent Pt layers altered upon SO₂ adsorption (see Table 4.9).

4.4.2 Bader Analysis of PtSO_{2(ad)}

To characterise the most favourable adsorption geometry, i.e. η²-FCC-S_bO_a, further, BC analysis was performed in order to comprehensively describe the electronic interaction between Pt(111) and the adsorbed SO₂. A charge iso-surface (Figure 4.9), to graphically present the obtained BC differences for the most favourable SO₂ adsorption geometry (Figure 4.6a), was constructed.

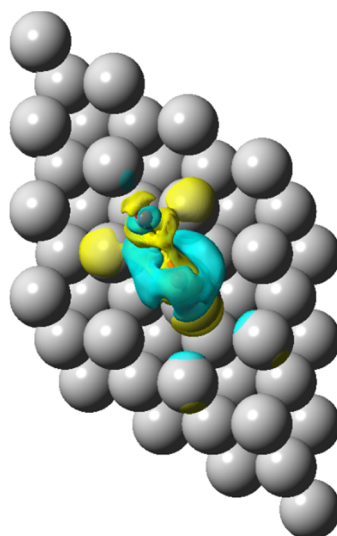


Figure 4.9: Surfaces of charge density difference maxima ($0.023474 \text{ e}^- \cdot \text{\AA}^{-3}$) in $\text{PtSO}_{2(\text{ad})}$ FCC- η^2 - S_bO_a . (Positive, i.e. a loss of negatively charged electron density, and negative, i.e. a gain in negatively charged electron density, maxima are indicated by teal and yellow respectively.)

Since a decrease in the electron density (i.e. positive charge shift) on Pt(111) results in a decrease of Pt d-electron availability for interaction with H_2O orbitals, it subsequently compromises the effective splitting of H_2O into H_2 and O_2 (reaction 4.1 and 4.14). The BC differences for the individual adsorbate atoms and Pt of the $\text{PtSO}_2 \eta^2$ -FCC- S_bO_a system are summarised in Table 4.10. A significant depletion in charge density of Pt(111), specifically for the top layer Pt atoms in closest proximity to SO_2 was observed.

Table 4.10: Bader Charge properties of atoms in the isolated molecule in comparison to the adsorption system in Figure 4.9

Species	$\text{BC}[\text{X}]_{\text{pristine}}$ surface/isolated adsorbate (e^-)	$\text{BC}_{\text{adsorbed}}$ (e^-)	$\Delta\text{BC}[\text{Pt}]$ (e^-)	Interpretation of ΔBC
Pt(111)	640.00	639.50	-0.50	Decrease
S_b	3.59	4.01	+0.43	Increase
O	7.22	7.36	+0.17	Increase
O_a	7.20	7.12	-0.10	Decrease

A homogenous distribution of electrons was observed in Pt(111) (see Table 4.3), however, the electron density and therefore the charge around each atom, may well differ upon adsorption of SO_2 depending on the distance between the SO_2 and the specific Pt atom.

From the BC differences, an effective charge transfer of 0.50e^- , from Pt(111) to SO_2 , occurred. This charge transfer is also visible in the isocharge-surface structure wherein Pt is characterised by a decrease in e^- density (teal) (see Figure 4.9). Moreover, a stronger electronic interaction between Pt and S, in comparison to the Pt-O interaction is suggested with S_b having a greater BC difference than O_a . This substantially high BC may have a significant influence on the required

electron transfer between Pt and H₂, and can further suggest that S_b acts as the prime electron-withdrawing atom of SO₂. This may be a result of S being in the 2.4+ partial oxidation state, because of polar covalent bonding, in the isolated SO₂ molecule. Since S is more electrophilic than the two O, the S orbitals contribute most towards the LUMO of SO₂. As a result, electron transfer from the Pt valence orbital to the S-like lowest unoccupied orbital of SO₂ occurred.

From the above results, a strong electronic interaction between Pt(111) and SO₂ was identified. This interaction was compared with those of co-adsorbed species in order to identify favourable reaction steps and intermediates.

Thus far, a rather comprehensive description of the adsorption behaviour of SO₂ on Pt(111) has been discussed (§4.3 and §4.4). However, to put these adsorption results in perspective and to comprehensively evaluate the strength of the interaction between Pt and SO₂, energies of other related sulphur oxides and other co-adsorbed molecule systems are needed. Thus, possible related molecular species are studied in the following sections of this chapter.

4.5 Adsorption of other SO_x species on Pt(111)

To further evaluate the possibilities of various reactions that adsorbed SO₂ might undergo on Pt(111), other sulphur oxides (SO_x; x = 1;3) were adsorbed onto Pt(111). Among these oxidised SO_x are neutral sulphur oxides, i.e. SO and SO₃, as well as ionic sulphur oxides, e.g. SO⁺ and SO₃²⁻. The adsorption properties of these species were subsequently further used to evaluate the energies of reactions 4.1 - 4.12.

4.5.1 Adsorption energies and geometries of SO_x (x=1,3)

The adsorption modes of SO and SO⁺ (they are symmetrically identical) on Pt(111) are displayed in Figure 4.10. The geometries where S is bound to the surface (Figure 4.10a and b), where both S and O is bound to the surface (Figure 4.10c and e) and O is bound to Pt (Figure 4.10d) were observed. In addition to adsorption energy, stereochemical properties such as bond length, bond angle and adsorption angle are presented.

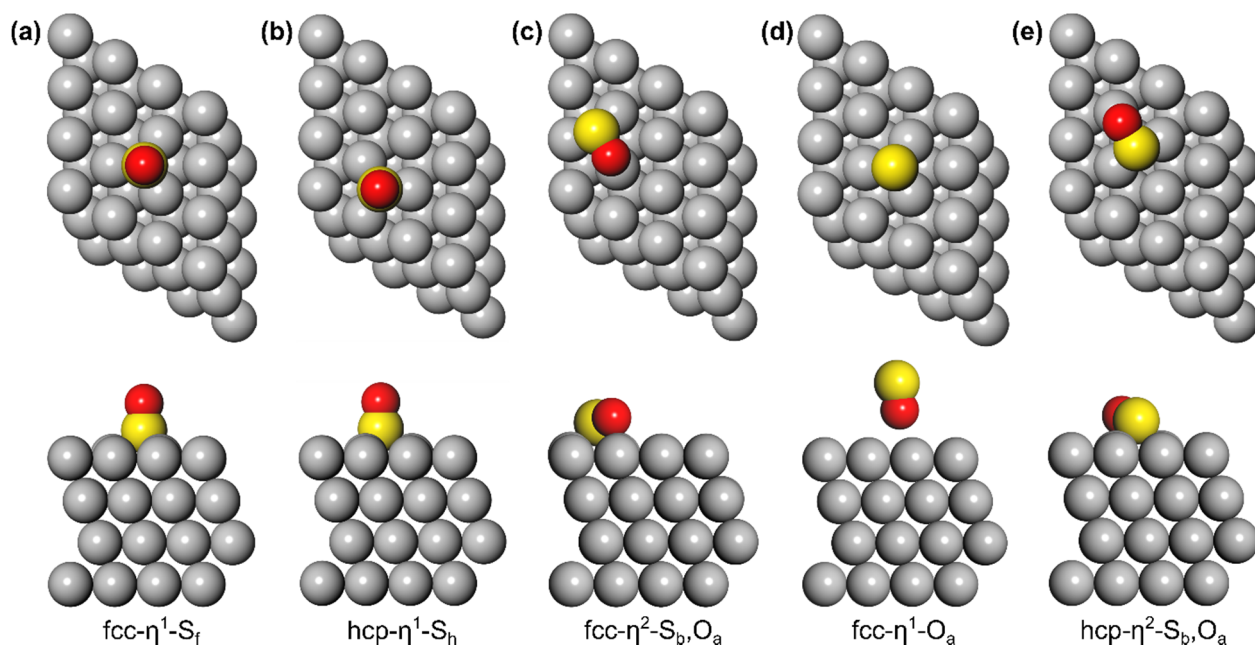


Figure 4.10: Top and side views of various SO and SO⁺ adsorption geometries on Pt(111)

The corresponding adsorption energies of the different PtSO_(ad) systems, as displayed in Figure 4.10a-e, are summarised in Table 4.11 and Figure 4.11.

Table 4.11: Adsorption energies and distances of different SO adsorption geometries on Pt(111)

Adsorption mode	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.10	$d_{\text{adsz}\perp}$ (Å)	θ_{ads} (°)	$E_{\text{free-ads-lit}}$ (eV)* [6,28]
FCC- $\eta^1\text{-S}_f$	-420.827	-3.370	(a)	1.509	90.0	-2.954 ^a
HCP- $\eta^1\text{-S}_h$	-420.683	-3.226	(b)	1.567	90.0	-2.809 ^a
FCC- $\eta^2\text{-S}_b,\text{O}_a$	-420.627	-3.171	(c)	1.947	0.0	-2.736 ^a
FCC- $\eta^1\text{-O}_f$	-417.682	-0.226	(d)	2.765	90.0	+0.299 ^b
HCP- $\eta^2\text{-S}_b,\text{O}_a$	-420.541	-3.084	(e)	-1.740	5.9	-2.684 ^a

^a. Happel et al 2011; ^b Lin et al. 2004

*Note that Lin et al.^a and Happel et al.^b used PW91 and not PBE

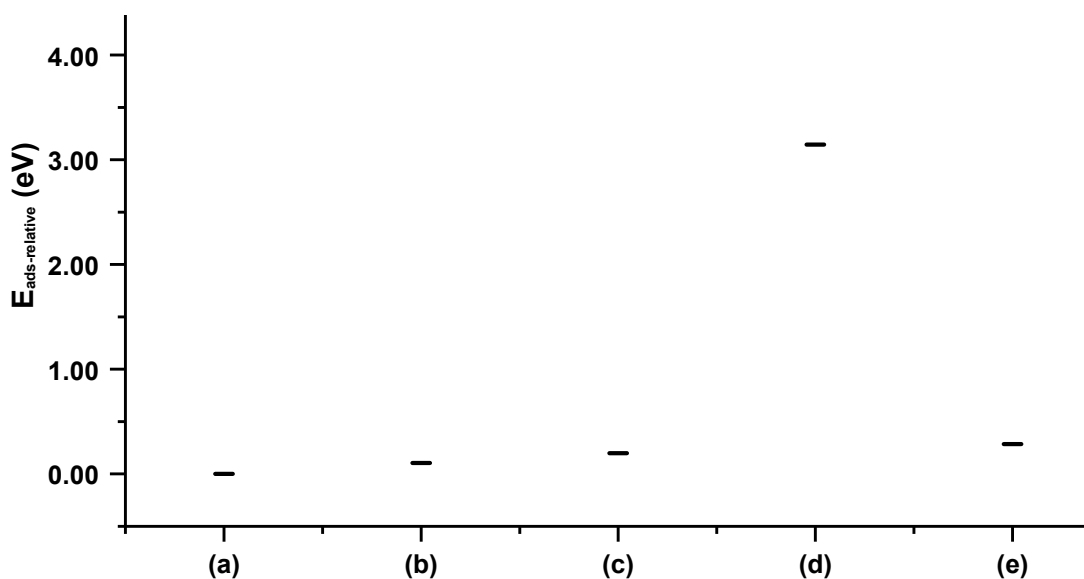


Figure 4.10

Figure 4.11: Relative adsorption energies of different SO adsorption geometries on Pt(111)

In Table 4.11 and Figure 4.11, it is evident that SO was adsorbed most favourably in the FCC- η^1 -S_f geometry on Pt(111) as displayed in Figure 4.10a. In addition, the vertical (z-direction) adsorption distance in this particular geometry is the shortest (1.509 Å) among the different adsorption geometries, being another characteristic of stronger bonding when compared to that displayed in Figure 4.10b (1.567 Å). The average vertical Pt-SO adsorption distance of the FCC- η^2 -S_bO_a adsorption geometry in Figure 4.10c is significantly greater than the geometries in Figure 4.10a and Figure 4.10b, and is further characterised by a slightly weaker adsorption energy (-2.736 eV). This result is in agreement with previous work regarding the adsorption of SO on Pt(111) [6,162]. Furthermore, all of the above-mentioned adsorption geometries of SO have a tendency to be adsorbed significantly stronger than SO₂ and the vertical adsorption distance d_{ads} of SO (1.509 Å) is shorter than that of SO₂ (1.685 Å). Another observation is the significantly weak adsorption energy of the FCC- η^1 -O_f mode, which is similar to earlier work [162].

In Table 4.12, the adsorption structural properties of the Pt FCC- η^1 -S_f SO_(ad) system (with literature [135] values in parenthesis) are listed.

Table 4.12: Structural properties of FCC- η^1 -S_f adsorbed SO

Structural property	η^1 S _{fl}
r(Pt-S) (Å)	2.269 (2.270)
r(S-O) (Å)	1.464 (1.496)

A notable observation regarding the adsorption of SO is that the S-O bond in SO, in contrast to the S=O bonds in SO₂, was decreased by 0.032 Å upon adsorption on Pt(111) (see Table 4.4 and Table 4.12), a tendency which has been observed previously for SO [28]. Furthermore, although this behaviour was the case for the most stable SO_(ad) mode, this is not necessarily true for all of

the possible SO adsorption modes such as FCC- η^2 -S_bO_a wherein the S-O bond length increased significantly by 0.068 Å [162].

In general, SO⁺ was adsorbed significantly stronger, on Pt(111), in comparison to both SO₂ and SO, with the FCC- η^1 -O_f geometry having an adsorption free-energy of -13.202 eV and a nearly-perpendicular adsorption angle of 87.6°. This may be ascribed to the ability of the half-filled SO⁺ valence orbital to undergo a strong electronic interaction with the Pt 5d electrons. This ionic-like interaction subsequently readily allows Pt electron acceptance by SO⁺, which strengthens the adsorption and can be described in more detail with Bader analysis (§4.5.2).

To evaluate reactions 4.3 and 4.4 on the pristine Pt(111), various SO₃ adsorption modes are presented in Figure 4.12. The most stable geometries are where all three O atoms are bound in atop positions on the surface (Figure 4.12a and b) or where two O atoms are bound to the Pt surface (Figure 4.12c and d). Note the difference between Figure 4.12a and b are the adsorption position of the S atom. In Figure 4.12a, the S is positioned in the HCP adsorption site in contrast to the FCC site in Figure 4.12b. The adsorption energies of the adsorbed SO₃ systems are listed in Table 4.13 and compared in Figure 4.13.

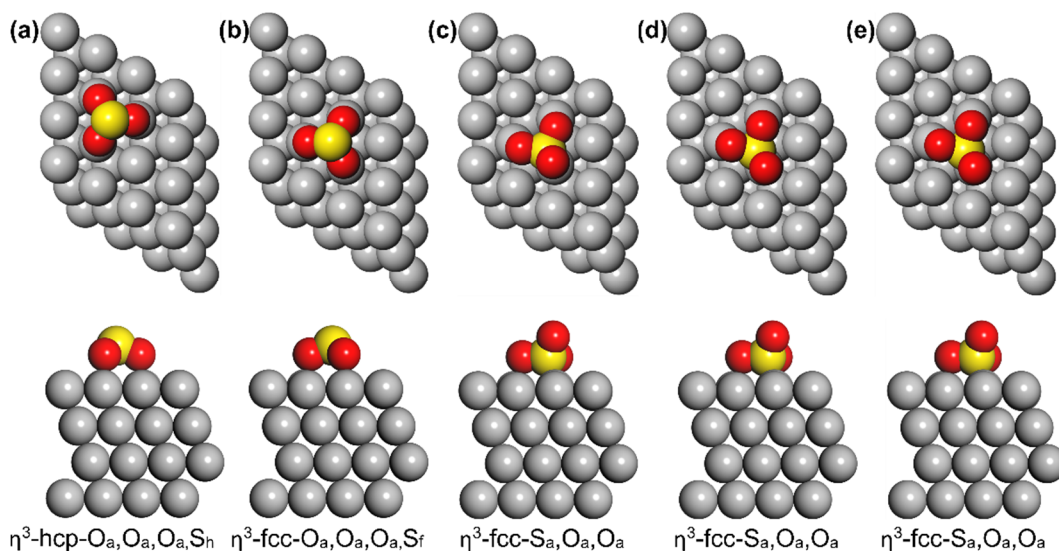


Figure 4.12: Top and side views of various SO₃²⁻ and SO₃ adsorption geometries on Pt(111)

The most favoured SO₃ adsorption geometry was identified as FCC- η^3 -S_aO_aO_a (Figure 4.12e) and is in accordance with literature regarding the adsorption of molecular SO₃ [45]. It is immediately noticed further that the adsorption of SO₃ on Pt(111), ($E_{\text{ads}} = +7.772$ eV) was significantly weaker than that of SO and SO₂. In fact, SO₃ desorption is highly favoured above adsorption and it can thus be concluded that, in the event wherein SO₃ is formed because of SO₂ oxidation, desorption of the product is highly probable. Furthermore, the molecular adsorption of

SO₃ on Pt(111) was highly unstable, and the dissociation of SO₃ to form SO₂ and SO during the adsorption process was highly favoured as another possible reaction on Pt(111).

Table 4.13: Adsorption energies of various SO₃²⁻ adsorption geometries

Adsorption mode	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.12
HCP- η^3 -O _a ,O _a ,O _a ,S _h	-425.389	+4.408	(a)
FCC- η^3 -O _a ,O _a ,O _a ,S _f	-425.414	+4.383	(b)
FCC- η^3 -S _a ,O _a ,O _a	-425.384	+4.412	(c)
FCC- η^3 -S _a ,O _a ,O _a	-425.872	+3.924	(d)

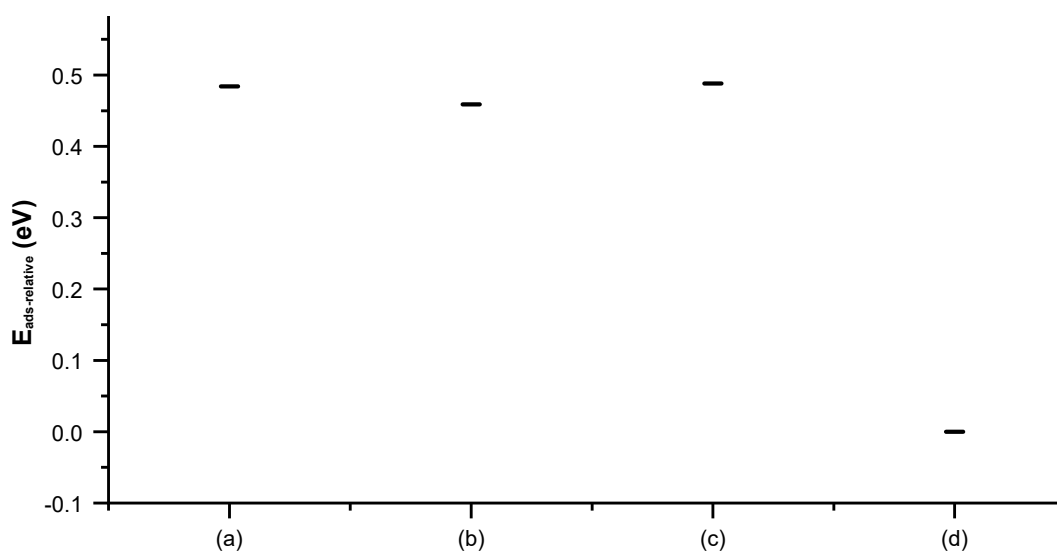


Figure 4.12

Figure 4.13: Relative adsorption energies of different SO₃²⁻ adsorption geometries on Pt(111)

Similarly to SO₃, SO₃²⁻ was preferentially adsorbed in the FCC- η^3 -S_a,O_a,O_a as well (Figure 4.12d). However, adsorption of SO₃²⁻ will not occur spontaneously since $E_{\text{free-ads}} > 0$. Therefore, in the event wherein SO₃²⁻ is formed as an unstable intermediate SO₂ oxidation product, a strong possibility does exist for SO₃²⁻ desorption to occur. Furthermore, since SO₃²⁻ is not readily available for Pt d-electron acceptance, it may account for the endergonic adsorption energy $E_{\text{ads}} \gg 0$ eV. Furthermore, in the absence of co-adsorbed H₂O, wherein only co-adsorbed O₂ is present, the formation of SO₄ as an SO₂ oxidation product, either with or without the formation of SO₃ as an intermediate, can occur. SO₃²⁻ is adsorbed weakly on Pt(111) (see Table 4.13). Furthermore, in the case where SO₃²⁻ is formed on the surface, it may react either immediately with possible co-adsorbed molecules such as H₃O⁺, or undergo desorption from Pt(111). It has further been found that SO₄ is preferentially adsorbed in the FCC- η^3 -O_a,O_a,O_a geometry with each O atom bonded to a separate Pt [28]. This implies that, upon oxidation on Pt(111), a structural rearrangement in SO₂ occurs wherein the bridged S_b detaches from the surface and migrates to an atop position on the Pt(111).

4.5.2 Bader analysis of adsorbed oxidised SO_x adsorption systems

Bader Charge (BC) analysis results are presented for the most stable geometries of PtSO_{x(ad)} systems, which may be formed as products or intermediate products in the SO₂ oxidation process as described by equations 4.1 – 4.12.

The BC results of the 64 Pt atoms collectively, as well as the BC of each atom in the most favourable adsorbed SO_x adsorbate modes (x = 1; 3), are summarised in Table 4.14:

Table 4.14: Adsorbed SO_x Bader properties

Species	Atom	Adsorption geometry	BC _{isolated} (e ⁻)	BC _{adsorbed} (e ⁻)	BC[Pt] (e ⁻)	ΔBC[Pt] (e ⁻)
SO ₃ ²⁻	S	FCC-η ³ -S _a ,O _a ,O _a	3.34	3.58	641.01	+1.01
	O		8.05	7.14		
	O		7.31	7.14		
	O		7.30	7.14		
SO	S	FCC-η ¹ -S _f	6.86	4.97	640.02	+0.02
	O		5.14	7.01		
SO ⁺	S	FCC-η ¹ -S _f	6.71	6.96	639.02	-0.98
	O		4.29	5.02		
SO ₃	S _a	FCC-η ³ -S _a ,O _a ,O _a	2.60	7.06	640.04	+0.04
	O(1) _a		7.13	5.40		
	O(2) _a		7.13	5.41		
	O(3)		7.15	6.09		

From the BC analysis of FCC-η³-S_a,O_a,O_a adsorbed SO₃²⁻, on Pt(111), it is implied that the oxidation of the adsorbate takes place by electron transfer from SO₃²⁻ to Pt. The Bader value, in particular, implies the formation of FCC-η³-S_a,O_a,O_a adsorbed SO₃⁻_(ad) on the Pt surface without any significant structural change accompanying the formation of SO₃⁻. Furthermore, from the BC differences in Table 4.14 electron transfer does occur in this case during the redox reaction, specifically between an atop-positioned O_a of SO₃²⁻ and the corresponding O-bonded Pt surface atom, i.e. Pt + SO₃^{2-(g)} → Pt⁻ + SO₃⁻_(ad).

BC analysis of SO and SO⁺ was performed in order to evaluate the dissociation of SO₂ on Pt(111) and to aid in the determination if SO and O or SO⁺ and O⁻ are formed as dissociation intermediates. From the BC of the Pt and SO⁺ adsorbent, it is probable that transfer of a single electron from the Pt to the unoccupied π₁^{*} orbital of SO⁺ occurred, wherein the latter was reduced from SO⁺ to SO.

SO did not display any significant overall BC change during adsorption on pristine Pt(111). It did, however, undergo a substantial change in its intra-molecular electron distribution, wherein two

electrons were transferred from S to O, i.e. S becomes more electropositive and O more electronegative.

The high BC difference of SO^+ corresponded to a strong electronic interaction with Pt(111) and the strongly negative adsorption free-energy obtained for the FCC- $\eta^1\text{-O}_f$ geometry. Upon closer inspection of the BC differences of the individual atoms it is noted, in contrast to SO , that O displayed a greater BC difference than S. One may well expect this since, in SO^+ , O is more electrophilic than S and will thus act more readily as a d electron acceptor when SO^+ interacts with Pt(111). SO^+ also had a greater BC difference than SO_2 (see Table 4.10) implying that the former undergoes stronger electronic interaction with Pt. Furthermore, the adsorption of SO^+ may thus be described as forming bonds that are more ionic (chemisorption) in nature than the adsorption of SO_2 .

Upon observing the BC of SO_3 it is noted that all four SO_3 atoms experienced significant changes in their BC upon adsorption. However, the BC change primarily occurred intra-molecularly and little charge transfer occurred between Pt(111) and SO_3 .

4.6 Adsorption of H_2SO_y species ($y = 3, 4$) on Pt(111)

Thus far, only products that may form as a result of the interaction between SO_2 and O_2 on Pt(111) have been discussed. Thus, to investigate products that may form specifically as a result of the reaction between SO_2 and H_2O (and O_2 if present), both H_2SO_4 and H_2SO_3 were adsorbed on Pt(111). The formation of H_2SO_4 was specifically investigated since it has a significant further influence on the sulphur depolarised electrode (SDE) mass transportability [23].

The most stable H_2SO_4 adsorption mode was used to evaluate the oxidation reaction energies described in reactions equations 4.1 - 4.8 and 4.11.

4.6.1 Adsorption energy of H_2SO_4

The adsorption energies of cis- and trans- H_2SO_4 are presented and discussed in order to compare it with that of SO_2 . These energies were subsequently employed to evaluate the favourability of SO_2 oxidation with co-adsorbed H_2O and O_2 on Pt(111).

H_2SO_4 was adsorbed onto Pt(111), and the most energetically favoured adsorption geometry was used as a reference in the evaluation of reactions 4.1 - 4.8 and 4.11 on the Pt surface. The adsorption geometries of H_2SO_4 on Pt(111) are displayed in Figure 4.14a-l, respectively. Note that both cis- and trans- H_2SO_4 adsorption geometries are displayed in Figure 4.14 and furthermore that the number of possible adsorption geometries, differ for the two isomers.

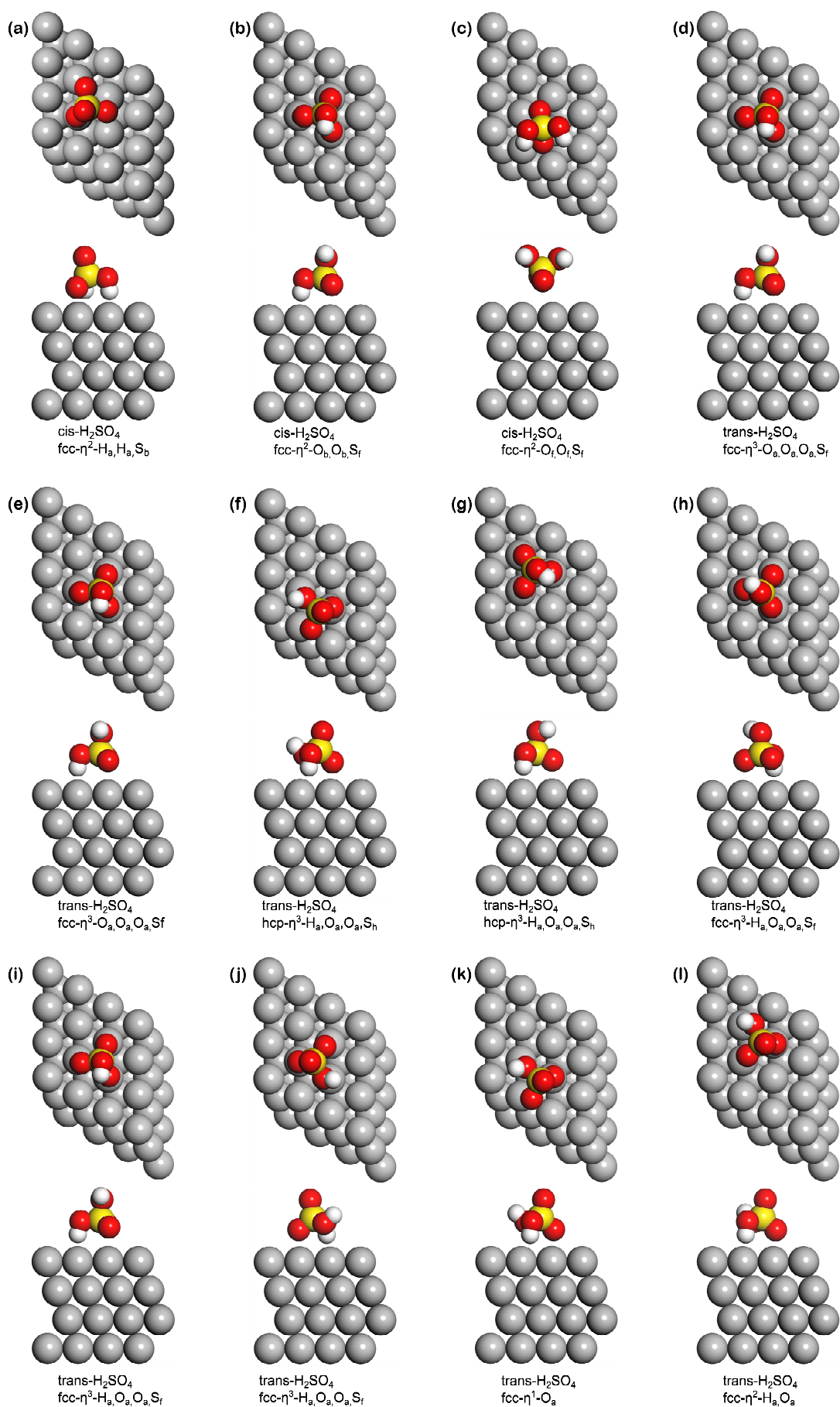


Figure 4.14: Top and side views of various cis- and trans-H₂SO_{4(ad)} adsorption geometries

The energies of various adsorption geometries for both cis- and trans-H₂SO₄ (Figure 4.14) are summarised in Table 4.15 and Figure 4.15:

Table 4.15: Adsorption free-energies of various cis- and trans-H₂SO_{4(ad)} adsorption geometries

Isomer	Adsorption geometry	$E_{free-system}$ (eV)	$E_{free-ads}$ (eV)	Figure 4.14
cis-H ₂ SO ₄	FCC- η^2 -H _a ,H _a ,S _b	-447.373	-0.921	(a)
cis-H ₂ SO ₄	FCC- η^2 -O _b ,O _b ,S _f	-447.213	-0.761	(b)
cis-H ₂ SO ₄	FCC- η^2 -O _f ,O _f ,S _f	-446.863	-0.411	(c)
trans-H ₂ SO ₄	FCC- η^3 -O _a ,O _a ,O _a ,S _f	-447.216	-0.710	(d)
trans-H ₂ SO ₄	FCC- η^3 -O _a ,O _a ,O _a ,S _f	-447.215	-0.709	(e)
trans-H ₂ SO ₄	HCP- η^3 -H _a ,O _a ,O _a ,S _h	-447.259	-0.753	(f)
trans-H ₂ SO ₄	HCP- η^3 -H _a ,O _a ,O _a ,S _h	-447.216	-0.709	(g)
trans-H ₂ SO ₄	FCC- η^3 -H _a ,O _a ,O _a ,S _f	-447.208	-0.702	(h)
trans-H ₂ SO ₄	FCC- η^3 -H _a ,O _a ,O _a ,S _f	-447.211	-0.705	(i)
trans-H ₂ SO ₄	FCC- η^2 -H _a ,O _a	-447.254	-0.749	(j)
trans-H ₂ SO ₄	FCC- η^1 -O _a	-447.254	-0.748	(k)
trans-H ₂ SO ₄	FCCHCP- η^2 -H _a ,O _a	-447.253	-0.747	(l)

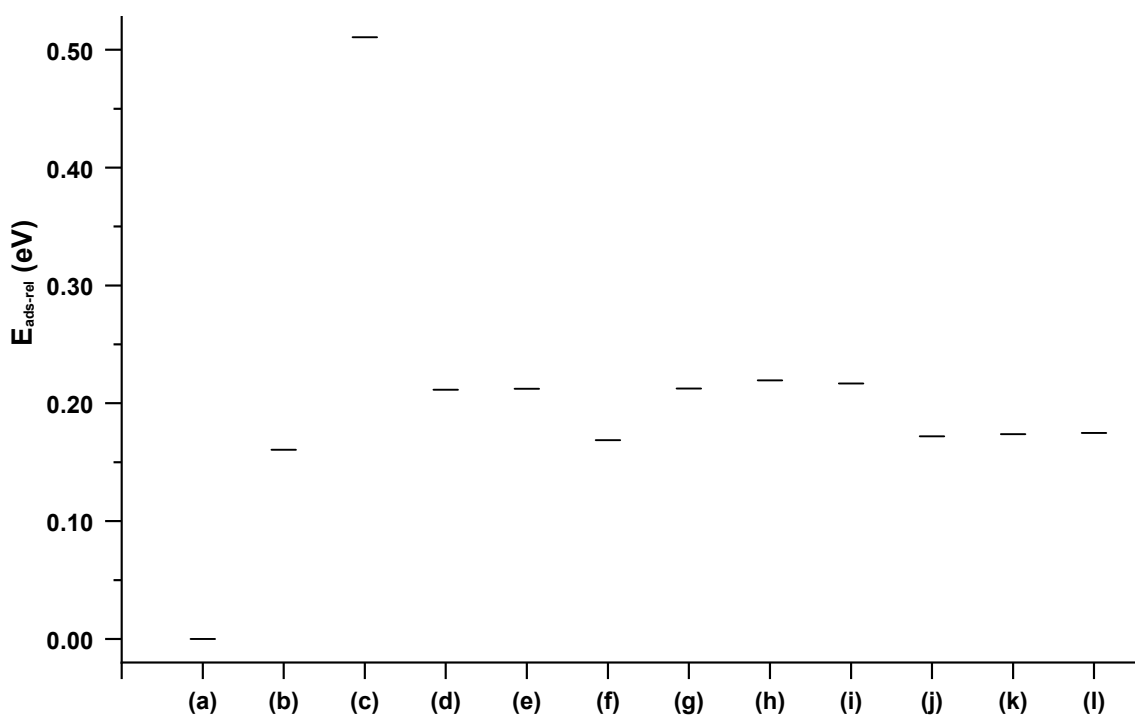


Figure 4.11

Figure 4.15: Relative adsorption energies of various cis- and trans-H₂SO₄ adsorption geometries on Pt(111)

From the energies in Table 4.15 and Figure 4.15, trans-H₂SO₄ is preferentially adsorbed in the HCP- η^3 -H_a,O_a,O_a-S_h geometry and cis-H₂SO₄ displayed a strong preference to be adsorbed in the FCC- η^2 -H_a,H_a-S_b geometry as displayed in Figure 4.14f,a respectively. All the H₂SO₄ adsorption

reactions (both for the trans- and cis-isomer) are, as in the case of SO₂, exergonic processes ($\Delta E_{\text{free-ads}} < 0$) and will therefore occur freely.

Even though the adsorption of both H₂SO₄ isomers led to PtH₂SO_{4(ad)} systems that were lower energy than the PtSO_{2(ad)} and PtSO_(ad) systems, both cis- and trans-H₂SO₄ were adsorbed weaker than SO₂ and SO. The adsorption energy of cis-H₂SO₄ (Figure 4.14a) is ~0.921 eV, which is still significantly weaker than SO₂ (~1.752 eV) and SO (~3.237 eV). Despite these observations regarding adsorption energy, PtH₂SO_{4(ad)} systems (for both the cis- and trans-isomers) still had lower system energies (in comparison to other PtX_(ad) systems). It therefore did provide enough reason to investigate the formation of H₂SO₄ on Pt(111) more thoroughly. Since the FCC- η^2 -H_a,H_a adsorption geometry was the most favourable, the formation of cis-H₂SO₄ on Pt(111) via the oxidation of adsorbed SO₂ (Reactions 4.1 - 4.3, 4.5 - 4.8 and 4.11) was investigated by using this adsorption geometry specifically.

In the FCC- η^2 -H_a,H_a adsorption geometry (Figure 4.14a) of cis-H₂SO₄, both H atoms are orientated toward Pt(111), suggesting that electron donation, from Pt to the H atoms, occur more readily. It can be noted as well that both H atoms of cis-H₂SO₄ are adsorbed in atop positions on top layer Pt and that electronic interaction between Pt and H is favoured.

The FCC- η^2 -O_f,O_f geometry (Figure 4.14c), of cis-H₂SO₄, had a significantly lower adsorption energy than those of the other adsorption geometries of cis-H₂SO₄. A specific characteristic that distinguishes the FCC- η^2 -O_f,O_f mode in particular from the other modes in Figure 4.14 is that none of the H-atoms of the cis-H₂SO₄ underwent significantly strong electronic interactions with Pt, since both H atoms are orientated away from the surface. A further consequence of this adsorption geometry is that no significant electron transfer from Pt to H can occur. Indeed, electronic interaction between Pt(111) and cis-H₂SO₄ in this adsorption geometry primarily occurs through the two double-bonded O atoms of the adsorbate. Since the two O atoms already have a noble-gas-like valence electron structure, its affinity towards receiving additional Pt electrons is lowered. The average vertical adsorption distance of the atoms of H₂SO₄ in Figure 4.14c, is in addition, significantly greater than that of the other geometries, which is a further indication of weaker interaction.

Upon adsorption on Pt(111) both cis- and trans-H₂SO₄ underwent structural changes wherein bond lengths and bond angles were changed. In §4.3.1 it was noted that the O-S-O bond angles in both cis-H₂SO₄ and trans-H₂SO₄ were such that the molecules form a near tetrahedral structure. When the structures of the adsorbed species are considered, some differences in bond angles were observed. In a similar manner, the bond lengths in H₂SO₄ (both in the cis- and trans-isomer) were distorted upon adsorption (Table 4.16).

Table 4.16: Structural properties of isolated and adsorbed cis- and trans-H₂SO₄

	$d_{\text{(ads)}} \text{ (Å)}$		Change = H ₂ SO _{4(ads)} – H ₂ SO _{4(g)}	
	trans	cis	cis	trans
H(1)-O(1)	1.03	1.01	0.03	0.05
H(2)-O(2)	0.98	1.01	0.03	0.00
S-O(1)	1.57	1.58	-0.03	-0.04
S-O(2)	1.61	1.58	-0.02	0.00
S-O(3)	1.44	1.47	0.03	0.01
S-O(4)	1.43	1.42	0.00	-0.01

A further observation is made upon closer inspection of Table 4.16, namely that the adsorption of cis-H₂SO₄ was stronger than that of trans-H₂SO₄; a tendency that can be ascribed to the stability of the isolated molecules. Since the trans-isomer of H₂SO₄ had a lower free-energy than the cis-isomer, the former was less reactive towards adsorption. In addition, upon adsorption the bond lengths in the cis-isomer were distorted to a greater degree than the trans-isomer. It is further concluded that the formation of adsorbed H₂SO₄ on Pt(111) and desorbed H₂, as a result of the reaction between SO₂ and H₂O on the surface, may be favoured above the formation of adsorbed H₂ and desorbing H₂SO₄.

4.6.2 Adsorption energy of H₂SO₃

H₂SO₃ is, in a similar manner to H₂SO₄, adsorbed in different modes on Pt(111) whereafter the calculated adsorption energies were used to identify the most favourable adsorption mode. Thereafter, the energy of the most favourable adsorption mode was used for further evaluation of reactions 4.1, 4.4, 4.8, 4.10 and 4.11 on Pt(111). The adsorption geometry of H₂SO₃ on Pt(111) is illustrated in Figure 4.16.

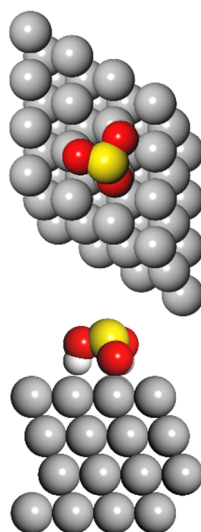


Figure 4.16: Top and side view of the FCC- η^3 -H_a,O_a,O_a adsorption geometry of H₂SO₃ on Pt(111)

The only optimised adsorption geometry obtained for H_2SO_3 was FCC- $\eta^3\text{-H}_a\text{,O}_a\text{,O}_a$ (-440.633 eV) and it had an adsorption energy of -1.069 eV. In comparison with SO_2 , H_2SO_3 was adsorbed relatively strong, and in comparison to cis- and trans- H_2SO_4 , H_2SO_3 was adsorbed very strongly on Pt(111). Since the adsorption energy of H_2SO_3 was strongly negative, desorption of H_2SO_3 from the Pt surface is highly unlikely. It is noted, that H_2SO_3 was, similar to H_2SO_4 , adsorbed as such that bond formation between the two H atoms and top layered Pt atoms occurred.

As a result of the high improbability of H_2SO_3 desorption ($E_{\text{free-ads}} \ll 0$), as well as the significantly high system energy in comparison to $\text{PtH}_2\text{SO}_{4(\text{ad})}$, a more favourable reaction possibility, is the immediate oxidation of adsorbed H_2SO_3 to form adsorbed cis- or trans- H_2SO_4 . Only after H_2SO_3 has undergone oxidation to H_2SO_4 , can desorption occur with less effort. Another possibility is that the adsorbed H_2SO_3 system is not an SO_2 oxidation intermediate product but rather a transition-like state since the former is a highly unstable species. In order to determine if this species is an intermediate or a transition-state, transition-state DFT modelling will be required. In addition, to evaluate the formation of adsorbed H_2SO_3 from $\text{SO}_{2(\text{ad})}$ and $\text{H}_2\text{O}_{(\text{ad})}$, it is required that the total energies of the $\text{H}_2\text{SO}_{3(\text{ad})}$ and $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption systems are compared. Therefore, the investigation of the co-adsorption properties of SO_2 with H_2O in further detail was required.

4.7 Bader analysis of adsorbed oxidised $\text{PtH}_n\text{SO}_{x(\text{ad})}$ systems

To further evaluate electron transfer during the oxidation of adsorbed SO_2 on Pt(111), BC analysis was performed for $\text{PtH}_n\text{SO}_{x(\text{ad})}$ systems. Electron transfer between Pt and H_nSO_x molecules, as well as between Pt and the respective atoms within adsorbed H_2SO_4 molecules, were investigated. The BC results of the $\text{PtH}_n\text{SO}_{x(\text{ad})}$ systems were subsequently compared with that of adsorbed SO_2 .

4.7.1 $\text{PtH}_2\text{SO}_{4(\text{ad})}$ Bader Analysis

Bader results of the cis- and trans- $\text{H}_2\text{SO}_{4(\text{ad})}$ adsorption systems, i.e. HCP- $\eta^3\text{-H}_a\text{,O}_a\text{,O}_a\text{-S}_h$ for trans- H_2SO_4 (Figure 4.14f) and FCC- $\eta^2\text{-H}_a\text{,H}_a\text{-S}_b$ for cis- H_2SO_4 (Figure 4.14a) are summarised in Table 4.17 and Table 4.18, respectively.

Table 4.17: Bader Differences in atoms as a result of the adsorption of cis-H₂SO₄ in the FCC- η^2 -H_a,H_a-S_b geometry

Atom in cis-H ₂ SO ₄	BC ^{isolated} (e ⁻)	BC ^{adsorbed} (e ⁻)	$\Delta BC = BC_{ads} - BC_g$ (e ⁻)
H(1)	0.35	0.40	+0.05
H(2)	0.37	0.40	+0.03
S	2.33	2.33	0.00
O(1)	7.30	7.21	-0.09
O(2)	7.20	7.22	+0.02
O(3)	7.26	7.24	-0.02
O(4)	7.19	7.27	+0.08
			+0.05

Table 4.18: Bader Differences in atoms as a result of the adsorption of trans-H₂SO₄ in the HCP- η^3 -H_a,O_a,O_a-S_h geometry

Atom in trans-H ₂ SO ₄	BC ^{isolated} (e ⁻)	BC ^{adsorbed} (e ⁻)	$\Delta BC = BC_{ads} - BC_g$ (e ⁻)
H(1)	0.33	0.42	+0.09
H(2)	0.35	0.33	-0.01
S	2.40	2.34	-0.05
O(1)	7.21	7.20	-0.01
O(2)	7.19	7.23	+0.04
O(3)	7.28	7.28	+0.00
O(4)	7.25	7.24	-0.01
			+0.05

From the Bader charge analysis, a net-charge transfer occurred from Pt to the adsorbed H₂SO₄. Furthermore, both forward, as well as back-donation of electron density, occurred. In FCC- η^2 -H_a,H_a-S_b adsorbed cis-H₂SO₄, back-donation of partial charge occurred from the Pt to both atop positioned H of H₂SO₄. It is further noted that the S of cis-H₂SO₄ did not experience any significant net-change in electron density (Table 4.17), however, a slight electron density change was indeed observed in trans-H₂SO₄ (Table 4.18).

4.7.2 PtH₂SO_{3(ad)} Bader Analysis

The BC of the single adsorbed H₂SO₃ molecule on Pt(111), in the FCC- η^3 -H_a,O_a,O_a geometry is summarised in Table 4.19.

Table 4.19: Bader Charges of H₂SO₃ in the gas and FCC- η^3 -H_aO_aO_a adsorbed system

Atom in H ₂ SO ₃	BC _{isolated} (e ⁻)	BC _{adsorbed} (e ⁻)	$\Delta BC = BC_{(ads)} - BC_{(g)}$ (e ⁻)
H(1)	0.572	0.416	+0.19
H(2)	0.519	0.413	+0.33
S	4.056	3.592	+0.19
O(1)	7.010	7.202	-0.46
O(2)	6.868	7.197	-0.10
O(3)	6.976	7.161	-0.16
			-0.02

The net charge transfer between Pt(111) and the adsorbed H₂SO₃ was very low ($\sim 0.02e^-$) with charge transferred from the adsorbate to the Pt(111). Similar to the observation of H in cis-H₂SO₄, charge transfer between Pt(111) and the H of H₂SO₃ occurred as such that the charge densities of the two H were increased.

The net charge transfer of H₂SO₃ was smaller than both H₂SO₄ isomers, and the weak charge interaction in H₂SO₃ corresponded to the significantly higher energy of the PtH₂SO₃ adsorption system (in comparison to PtH₂SO₄). As a result, if H₂SO₃ is formed as an intermediate in the oxidation of SO₂ with a first H₂O (i.e. from SO_{2(ad)} + H₂O_(ad) and SO_{2(ad)} + 2H₂O_(ad) co-adsorption systems), a high probability exists for an immediate reaction between H₂SO₃ and H₂O to occur, leading to the formation of H₂SO₄ and H₂. After the formation of H₂SO₄, dissociation may occur in the presence of H₂O, forming conjugated bases HSO₄⁻ and SO₄²⁻ in addition to the hydronium ion H₃O⁺.

4.8 Adsorption of ionic H_nSO₄^{x-} species on Pt(111) (n = 1; x = 1)

4.8.1 Adsorption of HSO₄⁻

Since ionic sulphates, such as the conjugated bases HSO₄⁻ and SO₄²⁻ of H₂SO₄, may be formed either as an intermediate or final dissociation products, the adsorption energies of the first ionisation step (formation of HSO₄⁻) is discussed. Various adsorption geometries of HSO₄⁻ on Pt(111) are displayed in Figure 4.17. Differences with respect to the adsorption position of bonded atoms, e.g. atop-positioned O_a, atop-positioned H_a as well as the position of the central S-atom relative to the surface, e.g. in the FCC position as in Figure 4.17b,c,e or the HCP position as in Figure 4.17a,d, are presented.

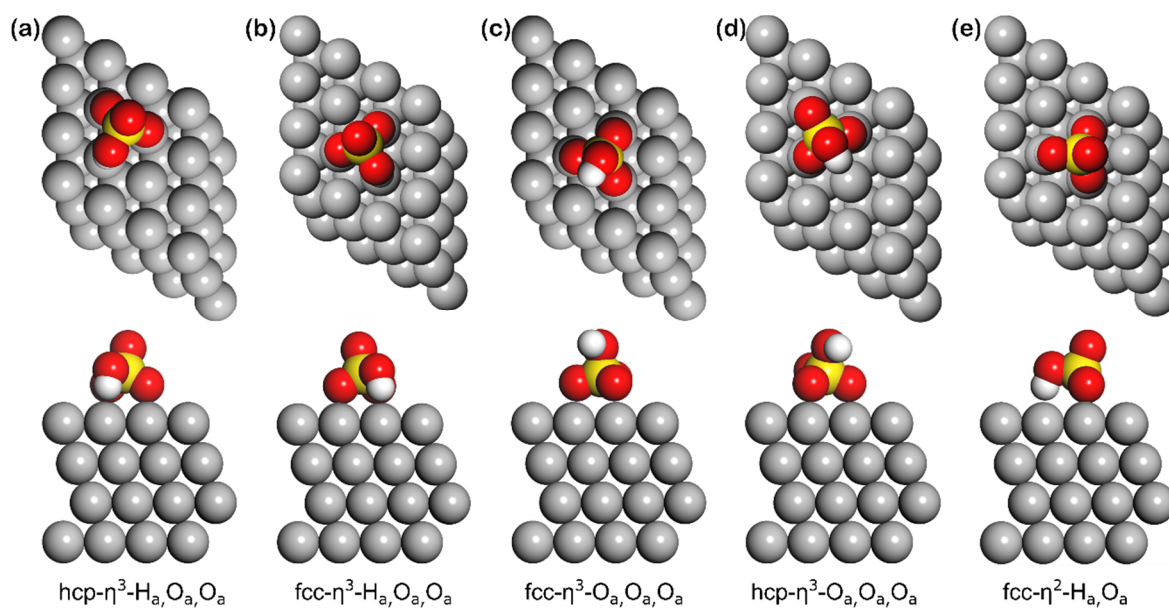


Figure 4.17: Adsorption geometries of HSO₄⁻ on Pt(111)

The energies of the above-displayed adsorption geometries are summarised in Table 4.20 and illustrated in Figure 4.18.

Table 4.20: Adsorption free-energies of various HSO₄⁻ adsorption geometries on Pt(111)

Adsorption geometry	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.17
HCP- η^3 -H _a ,O _a ,O _a	-441.179	+3.652	(a)
FCC- η^3 -H _a ,O _a ,O _a	-441.171	+3.660	(b)
FCC- η^3 -O _a ,O _a ,O _a	-440.882	+3.949	(c)
HCP- η^3 -O _a ,O _a ,O _a	-440.896	+3.935	(d)
FCC- η^2 -O _a ,O _a	-441.173	+3.658	(e)

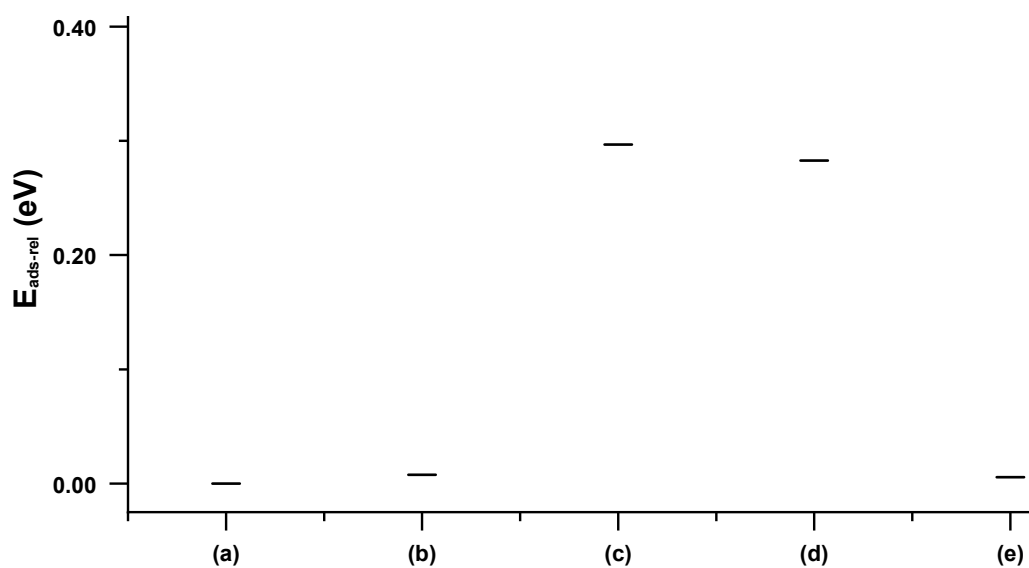


Figure 4.17

Figure 4.18: Relative adsorption energies of various HSO₄⁻ adsorption geometries on Pt(111)

The free-adsorption energies of all the geometries of HSO_4^- displayed in Figure 4.17 are $E_{\text{ads}} > 0$ and thus, adsorption will not occur spontaneously. Among the adsorption geometries, the HCP- $\eta^3\text{-H}_a\text{,O}_a\text{,O}_a$ adsorption geometry was characterised by the lowest adsorption energy. In addition, the total adsorption free-energy of the HCP- $\eta^3\text{-H}_a\text{,O}_a\text{,O}_a$ geometry (Figure 4.17a) was significantly higher (~ 5.806 eV) than the energy of the Pt FCC- $\eta^2\text{-H}_a\text{,H}_a\text{,S}_b$ cis- $\text{H}_2\text{SO}_{4(\text{ad})}$ system (Figure 4.14a). It should be remembered, however, that the H_2SO_4 adsorption system is neutral, whereas the HSO_4^- adsorption system is charged and therefore HSO_4^- , unlike H_2SO_4 , will tend not to accept any Pt d electrons. Despite this, the co-adsorption of H_3O^+ with HSO_4^- may significantly influence the energy and may change the energy to be comparable to that of an $\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption system, since both co-adsorption systems are neutral. Although the single adsorption of HSO_4^- on Pt(111) does not occur spontaneously, the presence of co-adsorbed H_3O^+ may stabilise the adsorbed HSO_4^- . Thus, in order to evaluate the dissociation of $\text{H}_2\text{SO}_{4(\text{ad})}$ on Pt(111), the analyses of $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ and $\text{HSO}_4^- + \text{H}_3\text{O}^+$ co-adsorption systems were required. Note that DFT calculations requires that a system contain at least one electron, however although adsorbed H^+ contain an electron, due to donation from Pt atoms, isolated gaseous H^+ does not contain any electrons. For this reason, the gas-phase dissociation energy of H_2SO_4 into HSO_4^- and H^+ cannot be evaluated. Therefore, it is better to calculate the energies of HSO_4^- and H_3O^+ with H_2SO_4 and H_2O as the initial reactants.

4.9 Adsorption of molecules that may be co-adsorbed with SO_2 on Pt(111)

Adsorption energies, distances and angles that have been calculated are represented and discussed. These results were henceforth used to evaluate the likelihood of the occurrence of the respective adsorption reactions and aided in the choice of system for evaluating the influence of co-adsorbed species for the SO_2 oxidation on Pt(111). The adsorption energies of molecules and ions that may undergo co-adsorption with SO_2 on Pt(111) were compared to that of SO_2 in order to identify the adsorption preference towards adsorbate identity on Pt(111).

4.9.1 Adsorption energies of molecules that may co-adsorb with SO_2

Adsorption properties of pre-adsorbed species determined as described in Chapter 3 are presented. Similar to SO_2 adsorption, the E_{ads} , adsorption distance d_z and adsorption angles of the respective adsorbates are discussed to comprehensively describe their interaction with pre-adsorbed SO_2 on Pt(111).

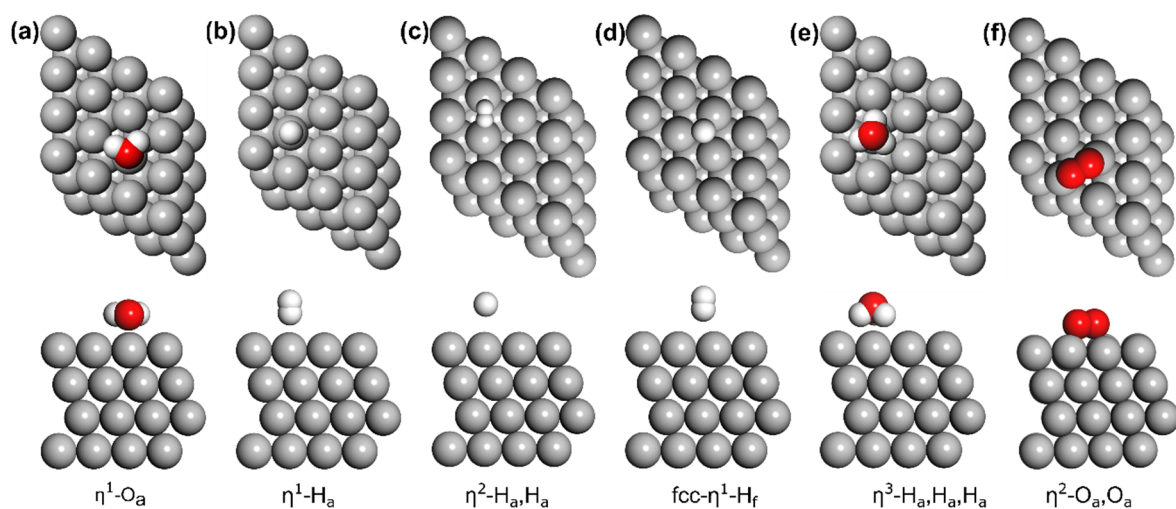


Figure 4.19: Adsorption geometries of various co-adsorbed species on Pt(111)

The free adsorption energies and structural properties of various molecular species that may form co-adsorbed systems, displayed in Figure 4.19, with SO₂ on Pt(111) are summarised in Table 4.21 and graphically compared in Figure 4.20.

Table 4.21: Adsorption Free-Energies and structural properties of various species that may be co-adsorbed with SO₂ on Pt(111), i.e. $X_{(g)} \rightarrow X_{(ad)}$

Species	Adsorption geometry	$E_{free-system}$ (eV)	$E_{free-ads}$ (eV)	$E_{free-ads-lit}$ (eV)	$d_{Ads,z}$ (Å)	θ_{Ads} (°)	Figure 4.19
H ₂ O	η^1-O_a	-423.030	-0.487	-0.464	2.390 (2.386)	2.7	(a)
H ₂	η^1-H_a	-415.191	-0.107		2.518	89.9	(b)
H ₂	η^2-H_a,H_a	-415.169	-0.084		3.098	0.0	(c)
H ₂	FCC- η^1-H_f	-415.185	-0.100		2.707	90.0	(d)
H ₃ O ⁺	η^3-H_a,H_a,H_a	-425.806	-8.292		2.332		(e)
O ₂	η^2-O_a,O_a	-419.069	-0.862		1.907 (1.08 ^a)	0.0	(f)

*Adsorption angle is measured with respect to the horizontal xy plane (i.e. Pt(111) plane)

*Literature distances in parenthesis ^a. Happel et al 2011; [6,14,135]

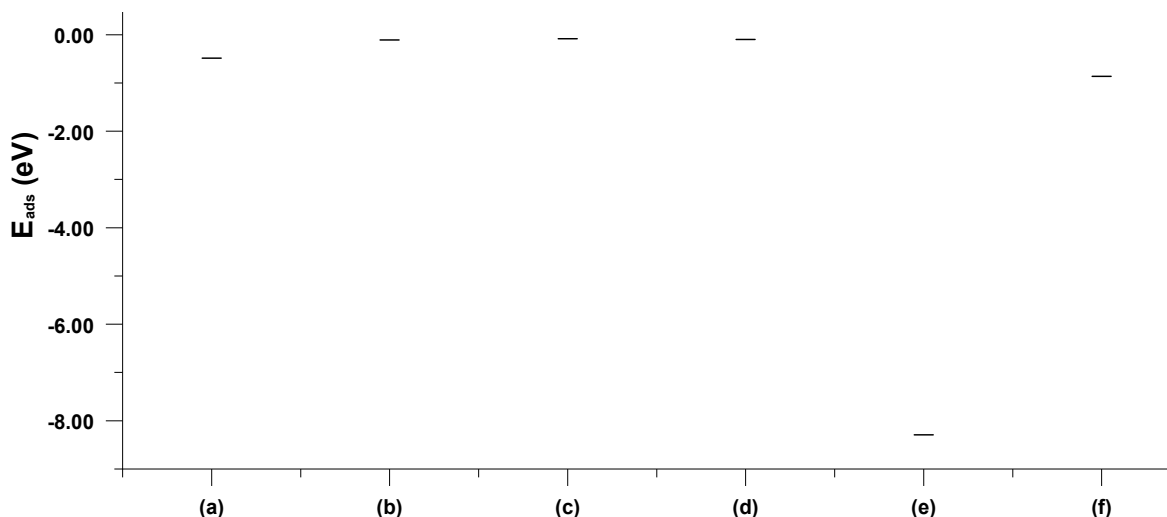


Figure 4.19

Figure 4.20: Adsorption free-energies of co-adsorbed species on Pt(111)

It has previously been found that H₂O is preferentially adsorbed in the η^1 -O_a adsorption geometry, with H₂O lying approximately parallel with the Pt surface [135,165,166]. For the η^1 -O_a adsorption geometry (Figure 4.19a) it was observed as well, with H₂O forming an adsorption angle of 2.67° with the Pt(111) plane. Since this adsorption mode was the most favourable among the adsorption possibilities, it was further used in the analyses of aSO_{2(ad)} + bH₂O_(ad) co-adsorption systems. A further observation is that SO₂ was adsorbed stronger than H₂O and may subsequently compromise the electronic interaction between Pt and H₂O in the HyS process.

The structural properties of isolated gaseous and adsorbed H₂O (on pristine Pt(111)) are summarised in Table 4.22. The positional displacement of the Pt atom is the displacement of the Pt atom from its original position (in the pristine Pt(111) system) to its final position when H₂O is adsorbed on the surface.

Table 4.22: Structural properties of isolated and η^1 -O_a adsorbed H₂O

Property	Isolated molecule	Adsorbed	Adsorbed Literature [14]
r[H(1)-O] (Å)	0.973	0.981	
r[H(2)-O] (Å)	0.973	0.981	
r[O-Pt(1)] (Å)		2.387	2.386
[Pt(3)-H(1)]		2.964	2.973
[Pt(2)-H(2)]		3.111	3.164
θ[H(1)-O-H(2)] (°)	104.5	104.8	104.9
φ[Pt-O-H] (°)	-	96.5	97.72

Upon adsorption, H₂O underwent structural changes wherein both O-H bonds elongated and the H-O-H bond angle, in contrast to the O-S-O angle in SO₂ (see Table 4.9), decreased. The difference in bond angle behaviour between SO₂ and H₂O was predominantly related to the

difference in their adsorption geometry preference, e.g. SO₂ was FCC-S_b,O_a perpendicularly adsorbed on Pt(111), whereas H₂O was parallel η^1 -O_a adsorbed. In comparison to SO₂, it is noticed that both H-O bonds in H₂O were stretched symmetrically by ~0.0082 Å, which is in contrast to the asymmetrical S=O bond elongation observed in adsorbed SO₂ (see Table 4.9) the latter being ascribed to the asymmetrical adsorption geometry of SO₂ (FCC-S_b,O_a).

H₂ was preferentially adsorbed onto Pt(111) in the η^1 -H_a geometry and was more weakly adsorbed than both SO₂ and H₂O (see Table 4.8). The η^1 -H_a adsorption geometry of H₂ was further characterised by a nearly perpendicular Pt-H¹-H² adsorption angle (89.9°), and as a result, the electronic interaction occurred primarily between one top layer Pt atom and the directly bound H_a of H₂. In addition, the vertical adsorption distance of H₂ (2.512 Å) was greater than that of H₂O (2.387 Å), which is a further indication of weaker surface-adsorbate interaction in H₂ than in H₂O.

In addition to being adsorbed stronger than both H₂ and H₂O, the adsorption of O₂ on Pt(111) is, in terms of adsorption energy, comparable to SO₂ (Table 4.8 and Table 4.21). As a result, it may be expected that SO₂ will be adsorbed strongly in favour of H₂ and H₂O, but not as significantly in favour of O₂. Furthermore, adsorption of O₂ on Pt(111) took place preferentially in the η^2 -O_a,O_a geometry (Figure 4.19f).

Since, in co-adsorbed systems, the specific adsorption preferences of H₂, O₂, H₂O and H₃O⁺ might, as a result of adsorbate-adsorbate interaction, differ if co-adsorbed SO₂ is present, various combinations of co-adsorbed systems were studied.

4.9.2 Bader Analysis of molecules that may co-adsorb with SO₂

Bader charge (BC) analysis of pre-adsorbed systems were performed in order to compare the Pt SO₂ electronic interaction with other species that may be present in the HyS cycle, either as co-adsorbates or intermediates. The BC analyses of various co-adsorbed species are summarised in Table 4.23. Note that since $\Delta BC = BC_{PtX_{ad}} - BC_{Pt}$, a positive BC difference represents an electron gain by Pt, i.e. electrons are transferred from the adsorbate to Pt, and a negative BC difference corresponds to an electron loss, i.e. electron charge transfer from the Pt surface to the adsorbate (BC = Bader charge count).

Table 4.23: Bader charge of co-adsorbable species on Pt(111)

Species	Valence e ⁻ (BC _{isolated})	BC _{adsorbed} (e ⁻)	$\Delta BC[Pt]$	Literature [14]
H ₂	2.00	1.99	+0.01	
H ₂ O	8.00	7.91	+0.09	+0.09
O ₂	12.00	12.54	-0.54	
H ₃ O ⁺	8.00	10.24	-2.24	

The BC difference of H₂ indicates a weak interaction between Pt and H₂. A stronger electronic interaction was observed between Pt and H₂O. However, both H₂ and H₂O displayed significantly weaker interaction with the Pt surface than observed earlier for SO₂. In contrast, O₂ had a stronger interaction with Pt(111) in comparison to SO₂. H₃O⁺ displayed a significant BC difference wherein two electrons were transferred from Pt to the adsorbing H₃O⁺_(g) leading to the formation of H₃O⁻_(ad). The high BC difference observed for H₃O⁺ may well be ascribed to the positive charge on the ion, making it more affinitive towards accepting electrons from Pt.

All of the neutral molecules (with the exception of O₂), that do not contain any S atoms and that may be co-adsorbed with SO₂ on Pt(111) have relatively small BC differences and thus, in comparison to SO₂, all underwent relatively weak electronic interaction with Pt. It is furthermore observed that no significant electron transfer between the Pt and the neutrally charged co-adsorbates occurred. The fact that the charge transfer of O₂ is comparable to that of SO₂, does imply that SO₂ adsorption as well as the subsequent oxidation thereof, is significantly influenced by the presence (or absence) of pre-adsorbed O₂, which can be a topic for further investigation, in particular for investigating the oxidation reaction $2\text{SO}_{2(g)} + \text{O}_{2(\text{pad})} \rightarrow 2\text{SO}_{3(\text{ad})}$.

4.10 Adsorption energies of multiple co-adsorbed molecules on Pt(111)

Thus far, only the adsorption of single isolated adsorbates, wherein co-adsorption does not occur, have been discussed. In order to improve the description of co-adsorption behaviour, multiple SO₂ and H₂O were simultaneously adsorbed on Pt(111). Adsorption of various combined systems on Pt(111) was thus investigated. The energies of various arrangement possibilities are presented wherein the most favourable arrangements of each respective PtX_(ad)Y_(ad) system were identified and used for further analysis. The adsorption energies of these combined systems were subsequently used to evaluate the influence of pre-adsorbed SO₂ on the adsorption of H₂O.

Since it was determined in §4.4.1 that FCC-η²-S_bO_a (Figure 4.6a) and η¹-O_a are the most favoured adsorption geometries on Pt(111) for SO₂ and H₂O, respectively, the combined aSO_{2(ad)} + bH₂O_(ad) systems were analysed wherein SO₂ was FCC-η²-S_bO_a and H₂O η¹-O_a adsorbed.

4.10.1 Adsorption energies of 2SO₂ co-adsorption arrangements

The adsorption energies of various arrangements of two co-adsorbed SO₂ are presented. In each system, the optimal adsorption mode for each adsorbate species was used, i.e. FCC-η²-S_bO_a. The adsorption energies of the co-adsorption arrangements were calculated in order to investigate the influence of a pre-adsorbed SO_{2(ad)} molecule on the adsorption process of additional SO₂ molecules and to identify the most favourable adsorption arrangement and

intermolecular distance between the two SO_2 molecules. The various co-adsorption arrangements of two SO_2 molecules on $\text{Pt}(111)$ are presented in Figure 4.21. Although the adsorption geometry of the two co-adsorbed SO_2 molecules remains $\text{FCC-}\eta^2\text{-S}_b\text{O}_a$ in all possibilities (illustrated in Figure 4.21), the relative distance between the two SO_2 molecules as well as the relative orientation (nearest position atoms) of the two SO_2 molecules, differed among the arrangements.

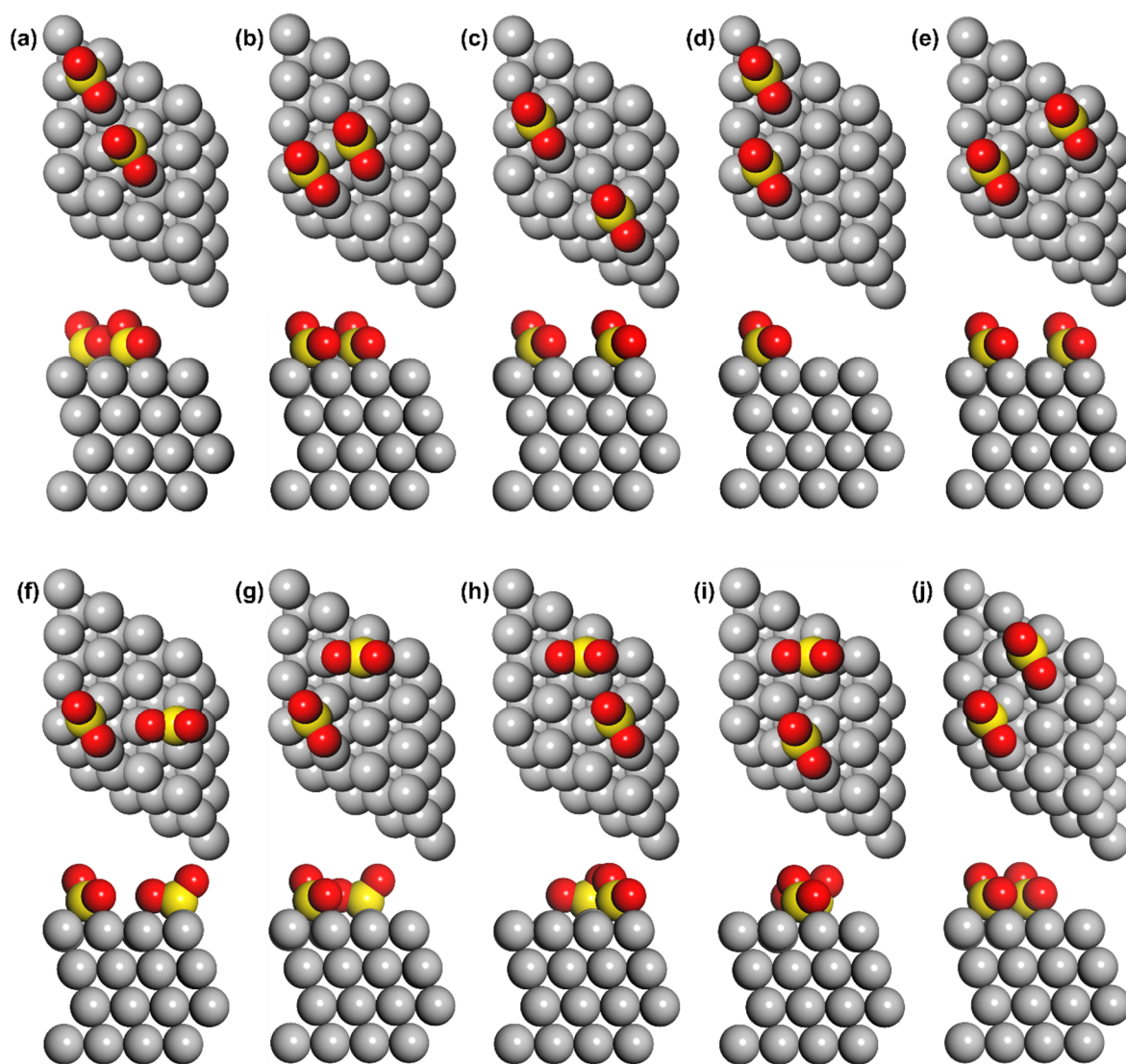


Figure 4.21: Top and side views of various arrangements of two $\text{FCC-}\eta^2\text{-S}_b\text{O}_a$ co-adsorbed SO_2 molecules on $\text{Pt}(111)$

The total system energies, as well as the calculated adsorption energies of the different arrangements of two co-adsorbed SO_2 $\text{FCC-}\eta^2\text{-S}_b\text{O}_a$ (Figure 4.21), are summarised in Table 4.24.

Table 4.24: Total Adsorption free-energies of two co-adsorbed SO₂ molecules on Pt(111)
i.e., $2\text{SO}_{2(g)} \rightarrow 2\text{SO}_{2(ad)}$

Arrangement	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.21
1	-445.649	-3.096	(a)
2	-445.387	-2.834	(b)
3	-445.715	-3.162	(c)
4	-445.757	-3.203	(d)
5	-445.790	-3.237	(e)
6	-445.758	-3.204	(f)
7	-445.721	-3.167	(g)
8	-445.666	-3.112	(h)
9	-445.785	-3.231	(i)
10	-445.714	-3.161	(j)

From the above, the adsorption energy of a second SO₂ molecule onto Pt(111), already containing one SO_{2(ad)}, leading to the formation of arrangement 5 (Figure 4.21e) was ~0.03 eV stronger than that of adsorption of a single SO₂ molecule on pristine Pt(111). This strengthening in the adsorption energy of the second SO₂ is a result of both the influence of the first SO₂ on the electron distribution of the top-layered surface Pt atoms as well as that of the direct SO_{2(ad)}-SO_{2(g)} interaction.

The most favourable adsorption arrangement, i.e arrangement 5 (Figure 4.21e) is, in comparison to the other arrangements, characterised by a weaker electronic interaction between the first SO₂ and the second SO₂. In arrangement 5 this repulsive intermolecular interaction stabilised the adsorption of both SO₂ molecules the most.

Adsorption arrangement 2 (Figure 4.21b) was ~0.40 eV higher in energy than arrangements 5 and 0.26 eV higher than the arrangement with the second highest energy, i.e. arrangement 1. Similar to arrangement 5, the two SO₂ molecules of arrangement 2 were adsorbed parallel to one another, but in this case at neighbouring adsorption sites (as opposed to Figure 4.21e). Since in both arrangements 2 and 5 the SO₂ were parallel with one another, the only distinctive difference between the two arrangements is the distance between the two SO₂ molecules. (The SO₂ molecules are closer to one another in arrangement 2 (3.11 Å) than in arrangement 5 (5.54 Å)). Therefore, it is probable that the repulsion between the two SO₂ was higher in arrangement 2 than in arrangement 5 which subsequently led to the higher energy of the former. Another possibility is the fact that in arrangement 2 a Pt atom was shared between the two co-adsorbed SO₂. Since the Pt atom was being shared, the electronic interaction between the Pt atom and

each of the two SO₂ was lower than in the case wherein a Pt atom underwent electronic interaction with only one S_b.

It is also observed that arrangements wherein atoms with the same electron negativity are located adjacent to one another, such as in arrangements 3 and 4 (Figure 4.21c,d), did not provide significantly strong electronic stabilisation of co-adsorbates, which is in contrast to the observation in arrangement 1 (Figure 4.21a). Arrangements 4 and 6 are particularly similar in terms of their adsorption energies despite their distinct difference in their SO₂ positions and relative orientation between the co-adsorbed molecules.

Arrangement 9 (Figure 4.21i) was similar in energy to arrangement 5 despite differing significantly in terms of structure. In this case, the free O of the first SO₂ was situated towards the atop positioned O_a of the second SO₂. In comparison to arrangement 8, SO₂-SO₂ repulsion was lower in arrangement 9, leading to the stronger adsorption energy in the latter. The adsorption energy of arrangement 10 (Figure 4.21j) was similar to that of arrangement 7. Herein, the atop positioned O_a of one SO₂ was located near the free O of the second SO₂, with weaker interaction between the two SO_{2(ad)}.

The reaction energies of the sequential adsorption of multiple SO₂ molecules, based upon arrangement 5, are summarised as follows:

Reaction				$\Delta E_{free-ads}$ (eV)	
SO _{2(g)}		→	SO _{2(ad)}	-1.752	
SO _{2(ad)}	+	SO _{2(g)}	→	2SO _{2(ad)}	-1.780

From the above, it is confirmed that the adsorption of a second SO_{2(g)} is indeed influenced by pre-adsorbed SO_{2(ad)} both in terms of adsorption energy as well as adsorption position relative to the first SO_{2(ad)}. In a similar manner the position and orientation of the first adsorbed SO₂ molecule is indeed influenced by the second adsorbing SO₂. Most notable, however, is that a significant increase in adsorption energy was observed for the second SO₂. This may be ascribed to an electronic Pt-SO_{2(g)} interaction as well as an electronic interaction between SO_{2(ad)} and SO_{2(g)}.

The influence of an adsorbed SO₂ on another SO₂ may well differ from the influence it has on other co-adsorbing species such as H₂O. Since H₂O is the second reactant of the HyS reaction, the influence of SO₂ on the adsorption behaviour of H₂O was investigated as well. These observations are subsequently discussed further in §4.10.2 - §4.10.7.

4.10.2 Adsorption energies of SO₂ + H₂O co-adsorption arrangements

In a similar manner to §4.10.1 wherein the co-adsorption of two SO₂ is discussed, co-adsorbed SO_{2(ad)} and H₂O_(ad) were investigated in order to evaluate the influence of pre-adsorbed SO_{2(ad)} on the adsorption process of H₂O. The adsorption energies of various unique arrangements of co-adsorbed SO₂ and H₂O molecules on Pt(111) are presented in Figure 4.22a - j. In each co-adsorption system, the optimal adsorption geometries, as identified in § 4.4 and §4.9 (i.e. FCC- η^2 -S_b,O_a for SO₂ and η^1 -O_a for H₂O), were used. Note that both the position and adsorption mode, i.e adsorption geometry, of SO₂ remained constant for all the arrangements and that the H₂O was moved to different positions relative to SO_{2(ad)}. Furthermore, in Figure 4.22, only unique adsorption arrangements were used and equivalent arrangements, which would thus be duplicating one another, were not calculated since they would have the same energy.

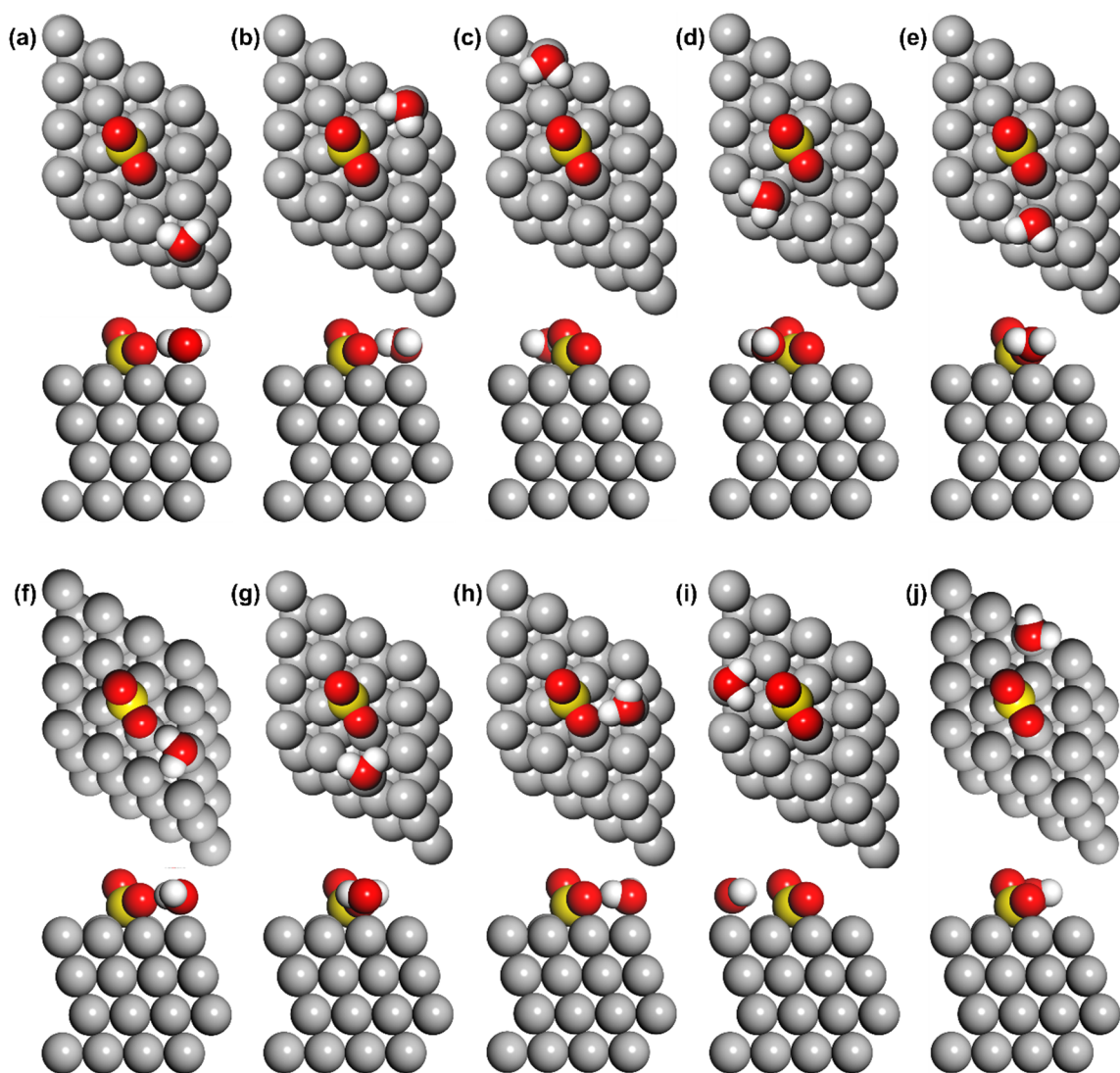


Figure 4.22: Top and side views of SO_{2(ad)} + H₂O_(ad) co-adsorption arrangements on Pt(111)

The total adsorption energies of the arrangements of co-adsorbed SO₂ (FCC- η^2 -S_b,O_a mode) and

H₂O (η^1 -O_a mode), i.e. $\text{SO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightarrow \text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$, are summarised in Table 4.25. Note that the intermolecular distance between SO₂ and H₂O was measured as the distance between those atoms closest to one another, e.g. in Figure 4.22d it is the distance between O_a of SO₂ and O_a of H₂O.

Table 4.25: Adsorption energies of SO_{2(ad)} + H₂O_(ad) co-adsorption arrangements

Arrangement	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	$d(\text{SO}_2\text{-H}_2\text{O})$ (Å)	Figure 4.22
1	-441.815	-2.306	5.141	(a)
2	-441.811	-2.302	3.214	(b)
3	-441.830	-2.320	3.515	(c)
4	-441.818	-2.309	3.096	(d)
5	-441.792	-2.282	3.400	(e)
6	-441.911	-2.402	2.019	(f)
7	-441.865	-2.355	2.563	(g)
8	-442.004	-2.495	1.770	(h)
9	-441.885	-2.376	2.587	(i)
10	-441.787	-2.278	3.512	(j)

A notable common feature among the SO_{2(ad)} – H₂O_(ad) co-adsorption arrangements in Table 4.25 is that they have strongly negative adsorption free-energies, i.e. they were all formed spontaneously as SO₂-H₂O co-adsorption products. The most favourable co-adsorbed SO₂-H₂O arrangement, when only energy is considered, was arrangement 8 (Figure 4.22h). Herein the SO₂ and H₂O were positioned in such an arrangement that the O_a of SO₂ was orientated towards one H of H₂O. Furthermore, in this particular arrangement, the SO₂ and H₂O were adsorbed relatively close to one another (1.77 Å). As a result, this arrangement was further stabilised by the formation of H-bonding between the SO₂ and H₂O.

Upon closer inspection of arrangements 1 and 2 (Figure 4.22a,b), it is noticed that in both structures the two H of H₂O are orientated towards the SO₂ and that subsequent H-bonding can occur. Two significant differences are, however, noticed as well. The first is the difference in intermolecular distance between SO₂ and H₂O (5.141 Å in Figure 4.22a and 3.214 Å in Figure 4.22b) and the second is the different angles between the two adsorbates. These differences in adsorbate distance and angle account for the observed adsorption energy difference between arrangements 1 and 2.

In comparison to the other $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption arrangements in Figure 4.22, the energy of arrangement 6 (Figure 4.22f) was notably lower. This significantly low energy may be ascribed to stronger electronic stabilisation in Figure 4.22f as a result of H-bonding between a hydrogen atom of H_2O and a lone electron pair on one of the O in SO_2 . Another distinctive property of Figure 4.22f is the intermolecular distance between the O_a of SO_2 and the nearest positioned H of H_2O . The short distance between the SO_2 and H_2O in this arrangement (the nearest positioned H of H_2O is 2.019 Å from O_a in arrangement 6), strengthens the intermolecular interaction between the two adsorbates and consequently provides further stabilisation in arrangement 6.

In contrast, when both H atoms in H_2O were orientated away from $\text{SO}_{2(\text{ad})}$, as in arrangements 4 and 5 (Figure 4.22d,e), co-adsorption of SO_2 and H_2O was comparatively weak. Within these arrangements, the subsequent SO_2 - H_2O interaction occurred primarily by means of an O-O interaction. Since the O atoms of the two molecules have the same electronegativity and subsequently also similar electron densities, as opposed to the large difference between that of O and H, the repulsion between adsorbates has a greater influence in these particular arrangements (Figure 4.22d,e). Furthermore, regarding intermolecular interaction, no H-bonding (H-bridging between O atoms) between SO_2 and H_2O was possible in these two arrangements (Figure 4.22d,e) since in both cases the two H (in H_2O) are orientated away from the SO_2 .

Another characteristic is noted on closer inspection of arrangements 6 and 7 (Figure 4.22f,g). Arrangements 6 and 7 have shorter intermolecular distances than 1 and 2 and may therefore be accompanied by stronger H-bonding than the latter. Both arrangements 6 and 7 have relatively low energies, which can be ascribed to the H-bonding interaction between the adsorbates. The difference between arrangements 6 and 7, however, is not only the specific orientation differences between H_2O and SO_2 , but also the intermolecular distance between the adsorbed SO_2 and H_2O . In arrangement 7 the H_2O is positioned further away from SO_2 than in arrangement 6 through which the H-bonding interaction in the former is weakened. The relative orientation between SO_2 and H_2O in arrangement 7 is similar to that in arrangement 1. Arrangement 7 does, however, have a 0.05 eV stronger adsorption energy than arrangement 1. The only significant difference between arrangement 1 and 7 is that the distance between SO_2 and H_2O is more than twice as long in arrangement 1 than in arrangement 7.

Arrangement 8 (Figure 4.22h) is similar to both arrangements 6 and 7. In this arrangement, however, the intermolecular distance between the O_a of SO_2 and one H of H_2O was only 1.77 Å (~0.25 Å closer than in arrangement 6) and was substantially lower in energy than the second and third most stable adsorption arrangements. This significant energy difference may well be a result of stronger SO_2 - H_2O interaction with strong H-bridging in arrangement 8. A further similarity

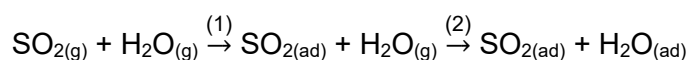
between arrangements 6 and 8 is that one H of the adsorbed H₂O is situated very near to the O_a atop positioned atom of SO₂, thus enhancing electronic interaction between the two adsorbates.

In addition to the intermolecular distance between the adsorbates, it has been noted that the adsorption energy is depended on the relative orientation of adsorbates as well. Since the electron densities of the two O atoms in adsorbed SO_{2(ad)} differ, the interaction between SO_{2(ad)} and H_{2O(ad)} depends on which O atom of SO₂ is orientated towards H₂O (i.e. the free O or the atop positioned O_a of SO₂).

A further observation, regarding the adsorption arrangements in Figure 4.22, is the adsorption angles of both SO₂ and H₂O, in comparison to adsorption angles on the pristine surface of the isolated molecules (see §4.4.1 and §4.9.1). When co-adsorption took place, the adsorption angle of H₂O changed, rotating the H atoms upwards away from the surface.

In contrast to H₂O, the adsorption angle of the SO₂ did not change significantly in the presence of co-adsorbed H₂O. The small change in adsorption angle leads to the conclusion that the adsorption of SO₂ is not as significantly influenced by pre-adsorbed H₂O than the influence experienced by adsorbing H₂O as a result of pre-adsorbed SO₂.

From the above, the two steps in the above-mentioned adsorption process, i.e. wherein SO₂ is adsorbed before H₂O, leading to arrangement 8, i.e.



can be described as follows. The energy of the first adsorption step (1) was -1.752 eV and that of the second adsorption step (2) was -0.743 eV. Thus, the adsorption of SO₂ was significantly stronger than that of H₂O. Recall that the adsorption energy of a single H₂O molecule on pristine Pt(111), i.e. in the absence of SO₂, was -0.487 eV. Thus, as a result of SO_{2(ad)}-H_{2O(g)} interaction, the adsorption energy of H₂O was increased by ~0.256 eV (~52%) if pre-adsorbed SO_{2(ad)} was present on Pt(111), that is, the adsorption of H₂O is significantly influenced by the electronic interaction between the H₂O and the pre-adsorbed SO₂.

If the obtained system energies of co-adsorbed SO₂ and H₂O are compared to that of H₂SO_{3(ad)} systems (§4.6.2), it is noted that SO_{2(ad)} + H_{2O(ad)} systems were lower in energy. The formation of H₂SO_{3(ad)} from co-adsorbed SO_{2(ad)} and H_{2O(ad)} therefore, does not occur spontaneously. Moreover, the oxidation of SO₂ via the reaction with a single H₂O will be improbable unless the H₂SO_{3(ad)} is not a reaction product but rather a transition-state species in the formation of adsorbed H₂SO₄.

The adsorption results displayed that H₂O adsorption on Pt(111) was substantially influenced by pre-adsorbed SO₂. The next step in evaluating SO₂-H₂O interaction on Pt(111) is to systematically add additional H₂O molecules to the SO_{2(ad)} + H₂O_(ad) system i.e. SO_{2(ad)} + 2H₂O_(ad) and SO_{2(ad)} + 3H₂O_(ad) in various arrangements. As in all studies (modelling or experimental), only one of the two variables (in this case the position of either the SO₂ or H₂O) was changed at a time to investigate the energetic properties of various adsorption arrangements.

4.10.3 Adsorption energies of SO₂ + 2H₂O co-adsorption arrangements

In the previous paragraph, the co-adsorption properties of one SO₂ with one H₂O were discussed. In order to describe the stoichiometric interaction between SO₂ and H₂O (of the HyS cycle) on the surface different SO_{2(ad)} + 2H₂O_(ad) co-adsorption arrangements and its corresponding adsorption energies are summarised in Figure 4.23 and Table 4.26, respectively. Since two H₂O were present in each of the adsorption arrangements displayed in Figure 4.23, numerous different hydrogen bonding formations were possible. As an example, two hydrogen bonds were formed between two H, one from H₂O(A) and the second from H₂O(B) and the O_a of SO₂ in Figure 4.23a, whereas only one hydrogen bond, between SO₂ and H₂O(A), was formed with no hydrogen bonding between SO₂ and H₂O(B), in Figure 4.23d. The formation of hydrogen bonds between the co-adsorbed molecules may, therefore, have a significant influence on the adsorption energy of a specific adsorption arrangement.

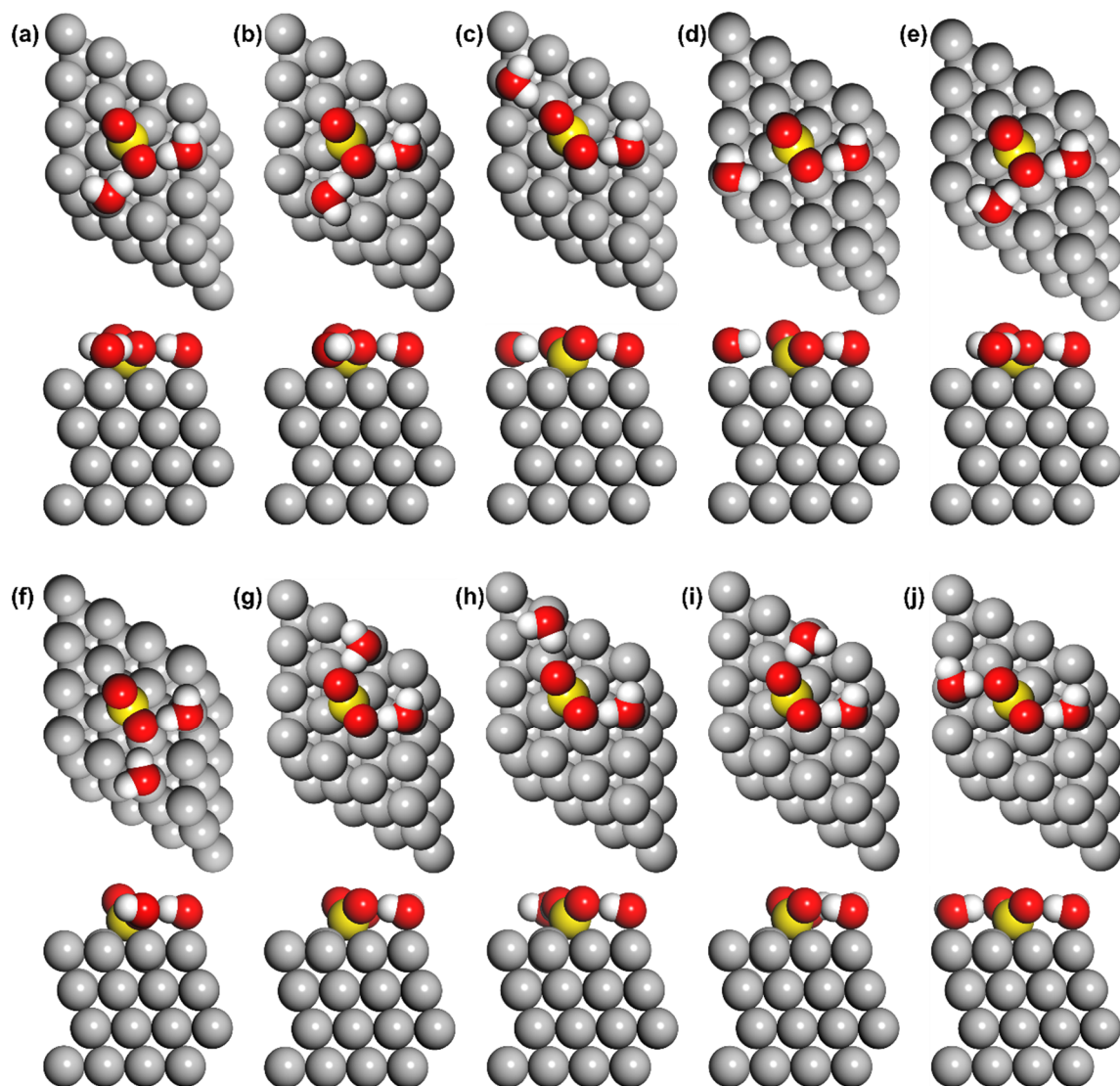


Figure 4.23: $\text{SO}_2 + 2\text{H}_2\text{O}$ co-adsorption arrangements on Pt(111)

It has been shown that the mobility of adsorbed H_2O was significantly higher than that of adsorbed SO_2 . Thus, in the co-adsorption arrangements displayed in Figure 4.23, the position of the FCC- $\text{S}_{\text{b}}, \text{O}_{\text{a}}$ adsorbed SO_2 , as well as the position of the first H_2O , were kept constant while the second H_2O molecule is moved to various adsorption locations relative to the former two adsorbates. For simplicity, it was assumed that the first adsorbed H_2O was stationary upon the adsorption of the second H_2O and, as in the case of SO_2 that no significant adsorbate migration of the former adsorbates occurred when the second H_2O was being adsorbed.

It should be noted further that both H₂O molecules were, in all of the arrangements in Figure 4.23, η^1 -O_a adsorbed as this has been found to be the preferred adsorption geometry. The energies of the various arrangements are accordingly summarised in Table 4.26. In addition, it should be noted as well that the energy of the SO_{2(ad)} + H₂O_(ad) system corresponded to that of arrangement 8 ($E_{\text{free}} = -442.004$ eV) in §4.10.2 as determined to be the most favourable SO_{2(ad)}-H₂O_(ad) co-adsorption arrangement. Note further that the energy of the un-adsorbed H₂O_(g) corresponded once again with the energy determined in §4.3.1.

Table 4.26: Adsorption energies of the SO_{2(ad)} + H₂O_(ad) + H₂O_(g) → SO_{2(ad)} + 2H₂O_(ad) reaction step leading to the arrangements in Figure 4.23

Arrangement	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.23
1	-456.273	-0.051	(a)
2	-456.356	-0.133	(b)
3	-456.819	-0.597	(c)
4	-456.714	-0.492	(d)
5	-456.279	-0.057	(e)
6	-456.794	-0.572	(f)
7	-456.960	-0.738	(g)
8	-456.814	-0.592	(h)
9	-456.912	-0.690	(i)
10	-456.993	-0.770	(j)

A significant variation in adsorption energies of the respective arrangements in was observed. Arrangements 7, 9 and 10 (Figure 4.23g,i,j) had significantly stronger adsorption energies than those of the other arrangements. In contrast, arrangements 1 and 5 (Figure 4.23a,e) had particularly weak adsorption energies. Another observation is made upon closer observation of arrangement 10. Although arrangement 10 (Figure 4.23j) was the most energetically stable, it had an adsorption energy that is rather insignificantly (~0.03 eV) stronger in comparison to the second most stable adsorption arrangement (arrangement 7). Thus, either arrangement 10 or arrangement 7 may be formed.

The strong adsorption energy of arrangement 10 may be explained by observing the relative adsorbate positions more thoroughly. In arrangement 10 the adsorbed H₂O were positioned around the SO₂ so that a hydrogen of one of each the two H₂O molecules was positioned close to an O of SO₂. Consequently, in this arrangement, both O of SO₂ formed H-bonding with an H₂O.

In arrangement 7, the adsorbed H₂O were positioned around the SO₂ so that a hydrogen of one of the two H₂O molecules was positioned close to, as well as orientated towards, the atop

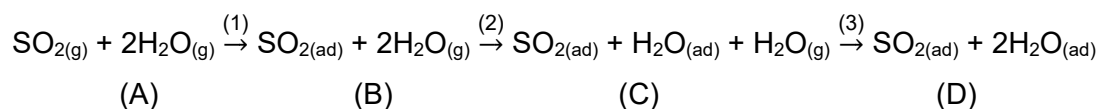
positioned O_a of SO₂. The second H₂O was adsorbed so that one of its H was orientated towards the second O of SO₂. Furthermore, the orientation of the two H₂O relative to one another was such that one H of the first H₂O was orientated towards the O of the second H₂O (see Figure 4.23g). Thus, in a similar manner to arrangement 10, H-bridging between the oxygen atoms of each of the two was H₂O possible providing further stabilisation in this adsorption arrangement.

Arrangement 9 (Figure 4.23i) was similar to arrangement 7, with the only difference being the orientation of the second H₂O. In arrangement 9 the H of each H₂O situated the furthest from SO₂ were orientated towards one another. Repulsion between the two H₂O may, as a result, be increased in arrangement 9, which subsequently led to the slightly weaker adsorption energy, in comparison to arrangement 7, being observed.

In addition to the classification as either strong or weak adsorption possibilities in Figure 4.23, some adsorption arrangements can be described as having intermediate adsorption strengths, i.e. arrangements 2 and 3 (Figure 4.23b,c). Herein, significant electronic interaction occurs between the SO₂ and only one of the H₂O, with the other H₂O positioned relatively far from the other two adsorbates. It is further noticed that one of the H₂O in arrangement 2 was rotated so that the O was lifted away from the surface. Consequently, the O_a was adsorbed significantly weaker in the preferred atop adsorption sites, which led again towards a weaker adsorption energy.

In both arrangements 1 and 5 (Figure 4.23a,e), the O_a atom of SO₂ was neighboured by at least one H of each of the two H₂O as opposed to arrangement 7 wherein only one H atom of one of the two H₂O was adsorbed near SO₂. Therefore, the most optimal stabilisation of the adsorption system is not provided if the adsorption locations of both H₂O is close to the O_a of SO₂. A possible reason for this observation could be the electronic interaction between Pt and the O_a of SO₂. Since this interaction affects the charge distribution, both around the SO₂ and Pt, the ability of the latter to interact with the atoms in H₂O is weakened. Another contributing factor is that the ability of the O_a of SO₂ to interact with a second H is significantly decreased by the interaction it has with the already present H of the first H₂O.

The energy of the two most favourable steps in the above-mentioned adsorption process, wherein the SO₂ adsorbed Pt(111) underwent further adsorption of two H₂O molecules, leading to arrangement 10 (Figure 4.23j), is summarised in Figure 4.24:



Adsorption System (Step)	E_{system} (eV)	$E_{\text{free-ads}}$ (eV)
A	-453.727	
(1)		-1.752
B	-455.480	
(2)		-0.743
C	-456.222	
(3)		-0.770
D	-456.992	

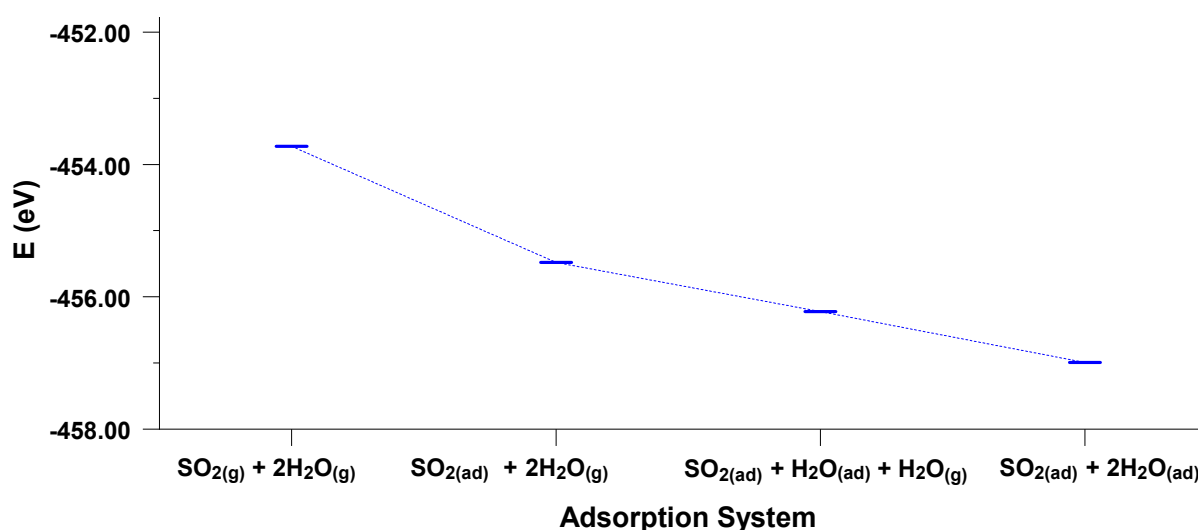


Figure 4.24: Energy diagram of sequential co-adsorption of one SO_2 with two H_2O on Pt(111) leading to $\text{SO}_{2(\text{ad})} + 2\text{H}_{2\text{O}(\text{ad})}$ adsorption arrangement 10 (Figure 4.23j)

In all but one of the adsorption arrangements consisting of a single SO_2 molecule co-adsorbed with two H_2O molecules, the adsorption energy of the second H_2O was smaller than the adsorption energy of the first. Recall from §4.10.2 that the adsorption of an H_2O on the surface, in the presence of pre-adsorbed SO_2 , was -0.743 eV and that the adsorption of a second H_2O is, insignificantly influenced being only ~ 0.027 eV ($< 1\%$) stronger than that of the first.

From the above, despite being insignificantly influenced by the adsorbed H_2O , the adsorption energy of a second H_2O was however susceptible to the presence of pre-adsorbed SO_2 . It should be noted, however, that in most of the arrangements displayed above, the presence of a co-adsorbed H_2O with the SO_2 does indeed appear to induce a slight decrease the interaction between the SO_2 and the second adsorbing H_2O . Thus, the observation that the second H_2O is adsorbed weaker than the first can, as a result, be described as a surface coverage effect of the $\text{SO}_{2(\text{ad})}$ rather than an influence of the first $\text{H}_{2\text{O}(\text{ad})}$. However, an exception does exist (arrangement 10), wherein the second H_2O was adsorbed stronger than the first. Thus, to

elaborate on these findings, further surface coverage systems are required with a greater number of adsorbates.

Thus far, a notable influence of co-adsorbed SO_2 and H_2O on the adsorption of a second H_2O has been identified. It has further been noted that the adsorption energy of H_2O is not influenced to a greater extent by pre-adsorbed SO_2 or H_2O . Thus far, adsorption systems containing only three or fewer adsorbed species have been discussed. In order to elaborate on these observations further, additional adsorbates were subsequently added to the $\text{SO}_{2(\text{ad})} + 2\text{H}_{2\text{O}_{(\text{ad})}}$ co-adsorption system.

4.10.4 Adsorption energies of $2\text{SO}_2 + \text{H}_2\text{O}$ co-adsorption arrangements

Co-adsorption systems, consisting of two SO_2 that are co-adsorbed with one H_2O , are presented. It is assumed that the two SO_2 were adsorbed before the H_2O and, in addition, that the adsorption locations of the two SO_2 did not change upon the adsorption of H_2O . The $2\text{SO}_{2(\text{ad})}$ system was, as a result, used as a reference in the calculation of H_2O adsorption energy and corresponds to that of arrangement 8 as determined to be the most stable in §4.10.1. Various $2\text{SO}_{2(\text{ad})} + \text{H}_{2\text{O}_{(\text{ad})}}$ co-adsorption arrangements are displayed in Figure 4.25 with their corresponding energies summarised in Table 4.27.

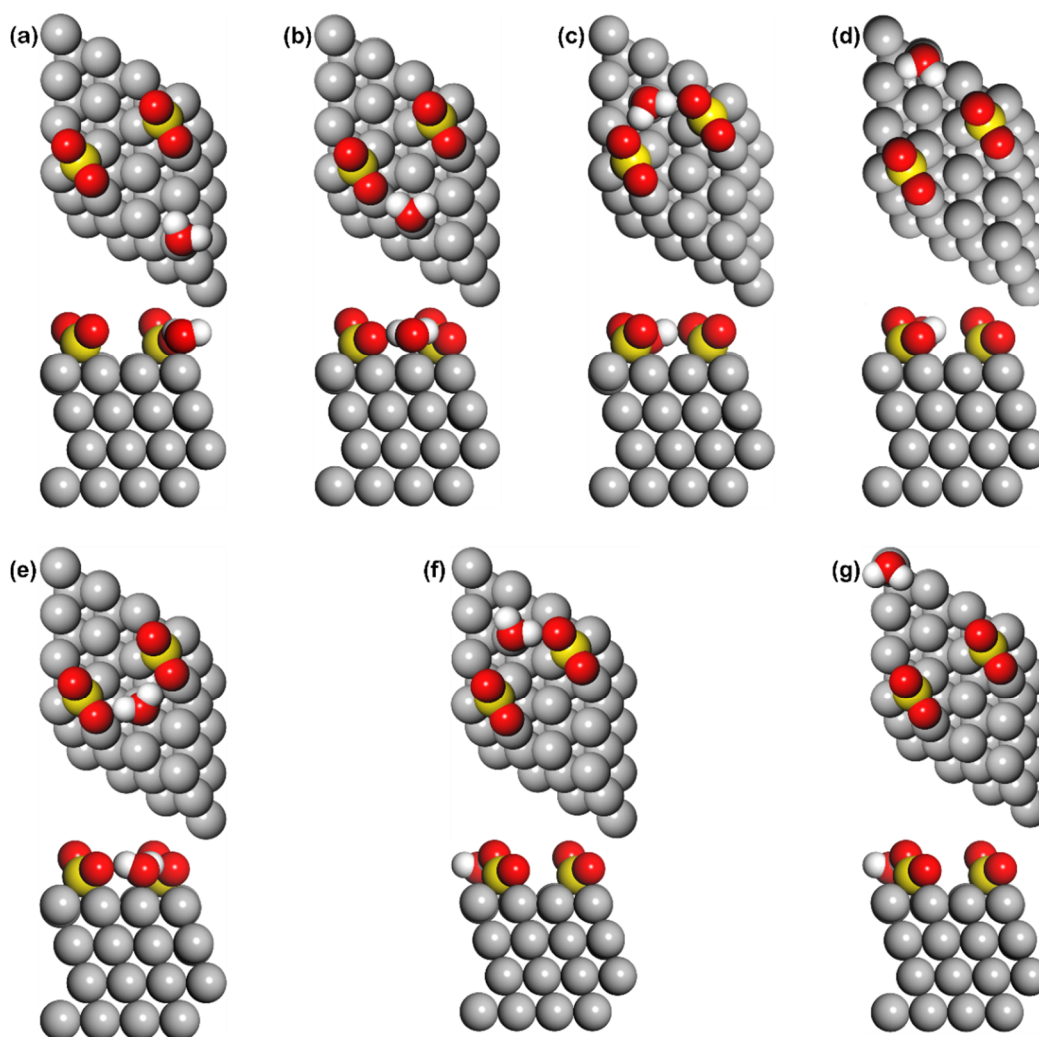


Figure 4.25: $2\text{SO}_2 + \text{H}_2\text{O}$ co-adsorption arrangements on Pt(111)

Table 4.27: Adsorption energies of co-adsorbed $2\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ arrangements i.e. $2\text{SO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{g})} \rightarrow 2\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$

Arrangement	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.25
1	-460.600	-3.828	(a)
2	-459.422	-2.650	(b)
3	-459.792	-3.021	(c)
4	-460.566	-3.795	(d)
5	-460.884	-4.112	(e)
6	-460.736	-3.964	(f)
7	-459.416	-2.645	(g)

All of the co-adsorption arrangements displayed in Figure 4.25 are formed exergonically ($E_{\text{free-ads}} < 0$). It is noticed, however, that some degree of variation in adsorption energy does exist among the different adsorption arrangements. For instance, is the energy of arrangement 5 was ~ 0.284 eV lower than arrangement 1, displaying a strong preference towards the former. Despite

the observations made regarding the total overall adsorption energy, however, the specific order wherein the respective adsorbates are adsorbed needs to be investigated further since the different adsorption steps may have energies that vary.

In the previous paragraph, it was stated that the order wherein molecules are adsorbed can influence the energies of intermediate adsorption steps. As a result, the adsorption of H₂O onto Pt(111) containing two adsorbed SO₂, with the same 2SO₂ adsorption arrangement as Figure 4.21e (see §4.10.1), was considered. The energies $E_{\text{free-ads}}$ for the 2SO_{2(ad)} + H₂O_(g) → 2SO_{2(ad)} + H₂O_(ad) adsorption step, leading to the arrangements in Figure 4.25, are summarised in Table 4.28.

Table 4.28: Adsorption energies of the 2SO_{2(ad)} + H₂O_(g) → 2SO_{2(ad)} + H₂O_(ad) step

Arrangement	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.25
1	-460.600	-0.592	(a)
2	-459.422	+0.586	(b)
3	-459.792	+0.216	(c)
4	-460.566	-0.558	(d)
5	-460.884	-0.876	(e)
6	-460.736	-0.727	(f)
7	-459.416	+0.592	(g)

Recall that the adsorption free-energy of H₂O in the presence of one adsorbed SO₂ was -0.743 eV (see §4.10.2). The presence of a second adsorbed SO₂, therefore, increased the adsorption energy of H₂O to -0.876 eV when leading to the formation of arrangement 5 (Figure 4.25e). The observed increase in adsorption energy of H₂O, when two SO₂ are present can be ascribed to the formation of H-bridging between H₂O and the atop positioned O_a of the first SO_{2(ad)}, but also H-bridging formation with O_a of the second SO_{2(ad)}. The energy of arrangement 5 was, in addition, significantly lower than that of arrangement 2 (Figure 4.25b) wherein H-bridging between H₂O and only one of the two SO₂, occurred.

In arrangement 1, the H₂O was adsorbed particularly far from both SO₂ with little to no H-bonding formed and thus further electronic stabilisation was unable to occur as well. In arrangement 3 (Figure 4.25c), both H of H₂O are orientated toward the two SO₂. This arrangement differs, however, from arrangement 5 as such that the two H are orientated towards the non-adsorbed O of SO₂ as opposed to arrangement 5 wherein the two H are positioned near the O_a of SO₂. The adsorption position of H₂O in arrangement 6 (Figure 4.25f) is identical to that of arrangement 3 (Figure 4.25c), although arrangement 6 had a significantly stronger adsorption energy. The only difference between the two arrangements is the positions of the two H relative to the SO₂. In arrangement 6, only one H is located near an O of one of the two SO₂, whereas both H of H₂O

are positioned near an O of each of the two SO₂. The observed energy difference is further indicative that H-bridging by both H₂O hydrogens stabilises adsorption less than when H-bridging is formed by only one of the two H.

In arrangement 4 (Figure 4.25d) the H₂O is positioned, similar to arrangement 1, far from the two SO₂, and is therefore characterised by comparatively weak electronic interaction. Arrangement 7 (Figure 4.25g), is similar to arrangement 4 (Figure 4.25d) with the H₂O being position slightly further from the two SO₂ molecules in the former. The difference in the distance between the H₂O and the two SO₂ has a significant influence on the adsorption energy, with arrangement 7 characterised by and adsorption energy 1.150 eV higher than arrangement 4.

In the discussion of Table 4.28 it was noted that the total collective adsorption energy of every arrangement was negative, $\Delta E_{\text{free-ads}} < 0$, and thus, that all of the arrangements in Figure 4.25 were formed freely. Despite this, the specific order wherein adsorbates were adsorbed proves to be of significant importance since the arrangements in Figure 4.25b,c and g are not formed spontaneously during the H₂O adsorption step since $\Delta E_{\text{free-ads}} > 0$ (see Table 4.28). Since arrangement 5 was significantly lower in energy than the other arrangements, it is possible that the latter may be formed as initial intermediate adsorption products which underwent structural rearrangement to subsequently form arrangement 5 (Figure 4.25e).

Thus far, the co-adsorption of two SO₂, as well as co-adsorption of two SO₂ with one H₂O were discussed. The sequential co-adsorption of two SO₂ with one H₂O can, in a similar manner as in §4.10.3 be summarised as follows:

Adsorption step		<i>E</i>_{free-ads} (eV)	
2SO _{2(g)} H ₂ O _(g)	→	SO _{2(ad)} + SO _{2(g)} + H ₂ O _(g)	-1.752 (1)
SO _{2(ad)} + SO _{2(g)} + H ₂ O _(g)	→	2SO _{2(ad)}	-1.780 (2)
2SO _{2(ad)} + H ₂ O _(g)	→	2SO _{2(ad)} + H ₂ O _(ad)	-0.876 (3)

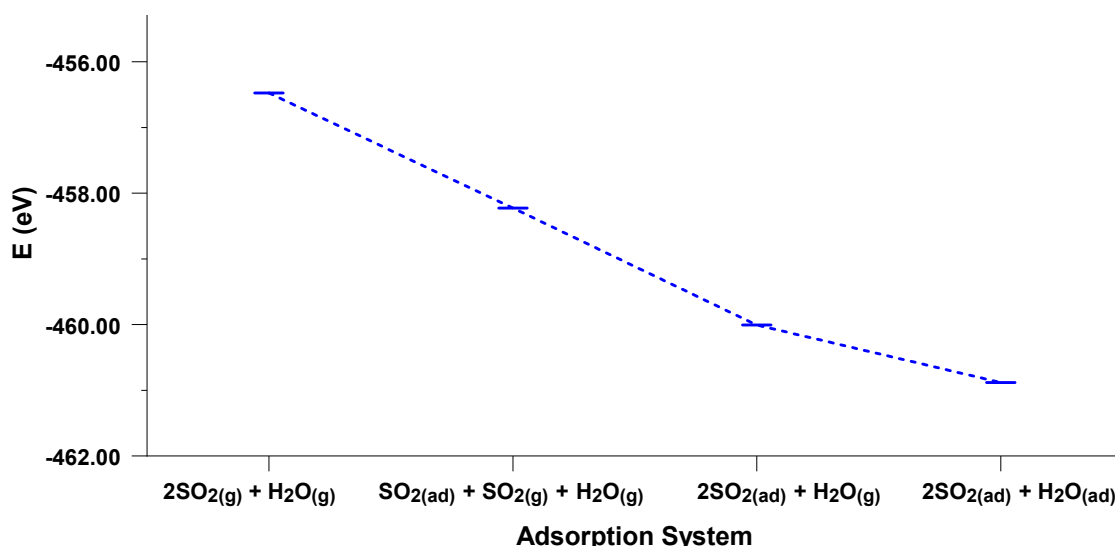


Figure 4.26: Sequential adsorption of two SO₂ with one H₂O on Pt(111)

In §4.10.2 it was noted that the molecular adsorption of H₂O on Pt(111) is enhanced by a pre-adsorbed SO₂ molecule, and from the above, enhanced further if a second additional pre-adsorbed SO₂ is present. From the latter reaction, the adsorption energy of H₂O was ~0.133 eV stronger when two, instead of one, pre-adsorbed SO₂, are present (Figure 4.26). However, despite stronger H₂O adsorption occurring when two SO₂ are present, H₂O was still adsorbed comparatively weakly on Pt(111), with an adsorption energy less than half of the first SO₂.

The adsorption of H₂O in the presence of two pre-adsorbed SO₂ was significantly stronger (~0.106 eV) than adsorption of H₂O in the presence of one pre-adsorbed SO₂ and one pre-adsorbed H₂O (see §4.10.3). All of the adsorption reactions of H₂O, which led to the most stable adsorption arrangements in §4.10.2, §4.10.3, and §4.10.4, were however characterised by a release of free-energy, i.e. $\Delta E_{\text{free-ads}} < 0$.

4.10.5 Adsorption energies of H₂SO₄ + H₂ co-adsorption arrangements

Since the required reaction products of the HyS cycle are H₂SO₄ and H₂, respectively, the adsorption energies of various cis-H₂SO₄ + H₂ co-adsorption arrangements (Figure 4.27) were calculated and summarised in Table 4.29. Note herein that the H₂SO₄ adsorption geometry corresponds to FCC- η^2 -H_a,H_a,S_b (Figure 4.14a) as determined to be the most favourable adsorption geometry of cis-H₂SO₄ in §4.6.1. Here, 12 possible arrangements are illustrated, each characterised by uniquely arranged cis-H₂SO₄ and H₂ on the surface. Note that since the adsorption of cis-H₂SO₄ on pristine Pt(111) is asymmetric, 12 different H₂ adsorption positions surrounding the adsorbed cis-H₂SO₄ are possible. It should be noted further, that, if the interaction between the adsorbed H₂SO₄ and the adsorbing H₂ is strong enough, the H₂ will not necessarily be adsorbed molecularly, but rather dissociative as in Figure 4.27a,g.

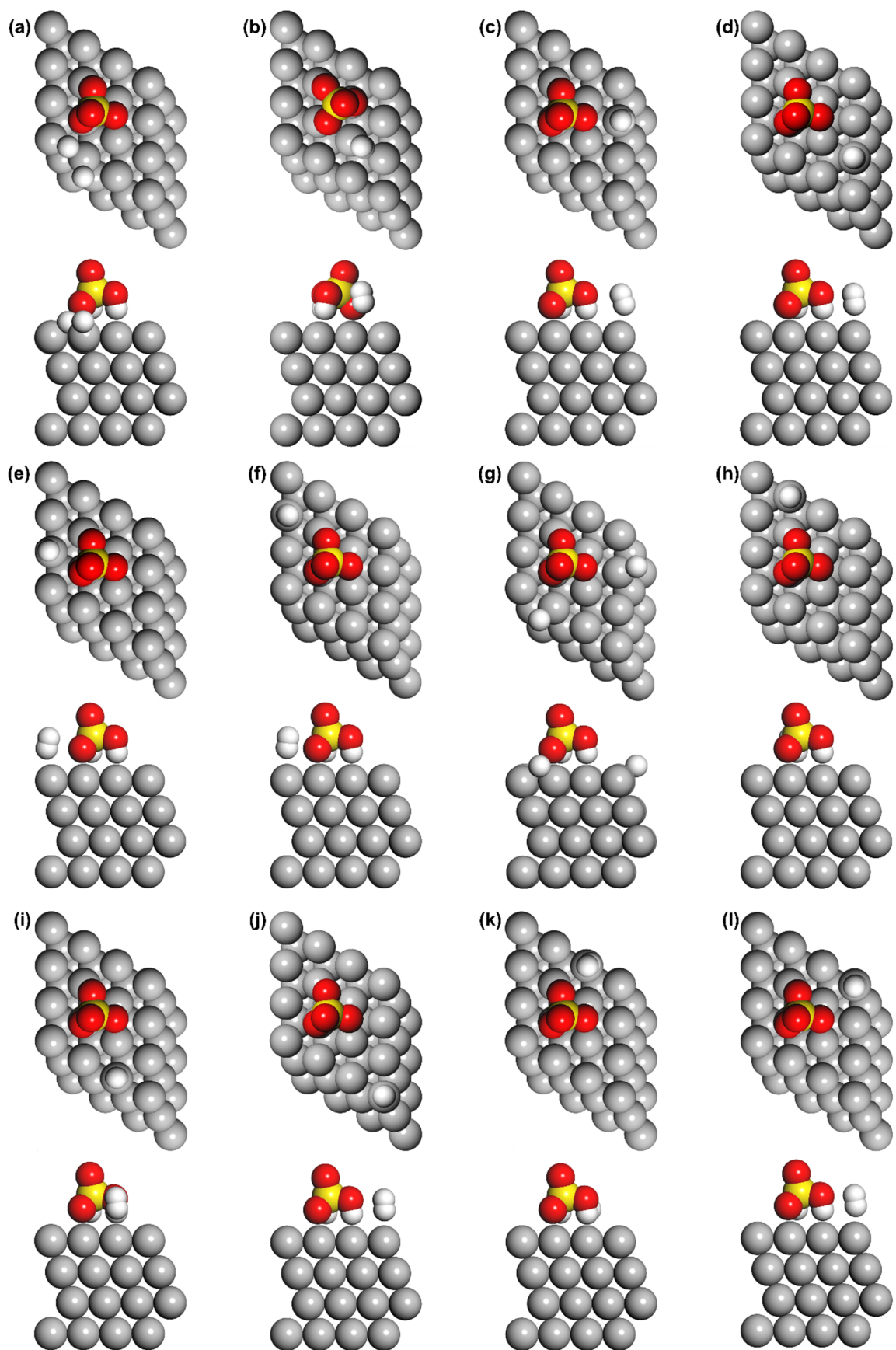


Figure 4.27: $\text{cis-H}_2\text{SO}_4 + \text{H}_2$ co-adsorption arrangements on $\text{Pt}(111)$

Table 4.29: Adsorption energies of cis-H₂SO₄ + H₂ co-adsorption arrangements on Pt(111)

Arrangement	$E_{\text{free-system}}$ (eV)	$E_{\text{free-ads}}$ (eV)	Figure 4.27
1	-455.134	-1.921	(a)
2	-454.243	-1.030	(b)
3	-453.856	-0.644	(c)
4	-453.870	-0.657	(d)
5	-453.884	-0.672	(e)
6	-453.853	-0.641	(f)
7	-455.171	-1.958	(g)
8	-453.846	-0.634	(h)
9	-453.708	-0.495	(i)
10	-453.843	-0.630	(j)
11	-453.863	-0.651	(k)
12	-453.858	-0.646	(l)

Arrangements 1 (Figure 4.27a) and 7 (Figure 4.27g) had the lowest energies, and both are distinguishable from the other arrangements in that the H₂ was dissociated, i.e. H₂SO_{4(ad)} + H_(ad) + H_(ad). For the initial co-adsorption (with molecular H₂) arrangement 2 (Figure 4.27b) had the strongest adsorption energy. A possibility for the formation of arrangements 1 and 7 is that both are preceded by adsorption arrangement 2 as an initial product, whereafter bond formation between the two H occurs to form H₂. Although Figure 4.27g was energetically the most favoured adsorption arrangement, the formation of this particular arrangement as the only product, from the reaction between SO₂ and 2H₂O, does have a dependency on the initial arrangement of SO₂ + 2H₂O. In §4.10.3 the most stable co-adsorption arrangement of one SO₂ with two H₂O was determined to be arrangement 10 (see Table 4.26). As a result, the formation of arrangements 1, 2 and 7, i.e. Figure 4.27a,b and g, may require the migration of H₂O on Pt(111), before the reaction between SO₂ and 2H₂O can take place. The possible necessity of H₂O migration can be identified, in future work, by means of transition-state analysis.

Recall that the adsorption energy of cis-H₂SO₄ on pristine Pt(111) was -0.921 eV (see Table 4.15). In the event wherein cis-H₂SO₄ and H₂ are sequentially adsorbed on Pt(111) the respective energies of the two adsorption steps leading to the formation of arrangement 7 (Figure 4.27g) may thus be summarised as:

Adsorption step		$E_{\text{free-ads}}$ (eV)
cis-H ₂ SO _{4(g)}	→	cis-H ₂ SO _{4(ad)} -0.921
cis-H ₂ SO _{4(ad)} + H _{2(g)}	→	cis-H ₂ SO _{4(ad)} + H _{2(ad)} -1.037

In contrast, in the event wherein H_2 is adsorbed before $\text{cis-H}_2\text{SO}_4$, the energies of the two adsorption steps are:

Adsorption step			$E_{\text{free-ads}}$ (eV)
$\text{H}_{2(\text{g})}$	$\rightarrow$	$\text{H}_{2(\text{ad})}$	-0.107
$\text{cis-H}_2\text{SO}_{4(\text{g})} + \text{H}_{2(\text{ad})}$	$\rightarrow$	$\text{cis-H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$	-1.852

From the above, the required energy for the desorption of H_2 with $\text{cis-H}_2\text{SO}_4$ remaining adsorbed on Pt(111) is thus +1.037 eV. In contrast, the required energy for the first step in the event wherein $\text{cis-H}_2\text{SO}_4$ is the first to desorb is +1.852 eV. Thus, it may be concluded, considering the adsorption energy, that H_2 desorption from Pt(111) tends to occur more readily than the desorption of the co-adsorbed $\text{cis-H}_2\text{SO}_4$. Furthermore, since H_2 is preferentially dissociatively adsorbed on Pt(111), i.e. Figure 4.27a,g, it is probable that these arrangements may serve as initial intermediate species, during the desorption of $\text{H}_{2(\text{g})}$. Furthermore, the formation of desorbed $\text{H}_{2(\text{g})}$ is likely to occur from the $\text{H}_2\text{SO}_{4(\text{ad})} + 2\text{H}_{(\text{ad})}$ initially formed on the surface because of the reaction between co-adsorbed SO_2 and two H_2O molecules.

4.10.6 Bader Analysis of the $\text{SO}_2 + \text{H}_2\text{O}$ co-adsorbed system

In order to identify the specific influence of SO_2 on the charge interaction between Pt and H_2O , Bader Charge analysis of $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption arrangement 8 (Figure 4.22h) was performed, and is summarised in Table 4.30. Recall from Chapter 3 that the BC-difference of a molecule or atom, between the adsorbed and gas phase, is defined as $\Delta\text{BC} = \text{BC}(\text{adsorbed}) - \text{BC}(\text{isolated})$ and therefore that $\Delta\text{BC} > 0$ corresponds to an electron gain and $\Delta\text{BC} < 0$ to a loss of electrons.

Table 4.30: Bader Charges and Bader Charge differences of atoms in the $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption system

Species		Pt BC pristine surface/ isolated molecule	BC in $\text{PtSO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$	ΔBC
64 Pt		640.00	639.77	-0.23
SO_2	S_b	3.59	4.06	+0.45
	O	7.22	7.16	-0.06
	O_a	7.20	7.14	-0.06
H_2O	H(1)	0.39	0.34	-0.05
	H(2)	0.39	0.34	-0.05
	O_a	7.22	7.20	-0.02

In §4.4.2 it was shown that the BC difference of SO_2 when adsorbed on pristine Pt(111) was $+0.50e^-$ i.e., electron density of SO_2 increases upon adsorption. Also from §4.9.2 that, in contrast to SO_2 , the BC difference of H_2O when adsorbed on pristine Pt(111) was $-0.09e^-$, i.e. electron density of H_2O decreases very slightly upon adsorption. When co-adsorbed SO_2 is present, the electron density of H_2O decreases by $-0.12e^-$. $\text{SO}_{2(\text{ad})}$ therefore induces a greater electron density decrease (BC decrease) in adsorbed H_2O . In addition, the BC difference of Pt(111) in the co-adsorption system is $-0.23e^-$. The charge transfer in the co-adsorption system is thus from Pt(111) as well as from $\text{H}_2\text{O}_{(\text{ad})}$ to $\text{SO}_{2(\text{ad})}$, i.e. a weaker electronic interaction between Pt and H_2O is formed.

Upon closer inspection of SO_2 , it is observed that the net electron density increase occurred primarily around the bridging S_b , and that a decrease in e^- density was observed for both O of SO_2 when H_2O was present. However, despite having a BC decrease in both O of SO_2 when H_2O was present, the increase in electron density around S_b was significantly greater, leading to an overall net electron density increase in SO_2 .

4.10.7 Bader Analysis of co-adsorbed $\text{SO}_2 + 2\text{H}_2\text{O}$ on Pt(111)

In §4.10.2 the energies of various $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption arrangements were discussed, whereafter co-adsorption arrangement 10 was identified as the energetically most stable arrangement. Thus, the subsequent BC analysis of this particular arrangement (Figure 4.23j) is summarised in Figure 4.28 and Table 4.31.

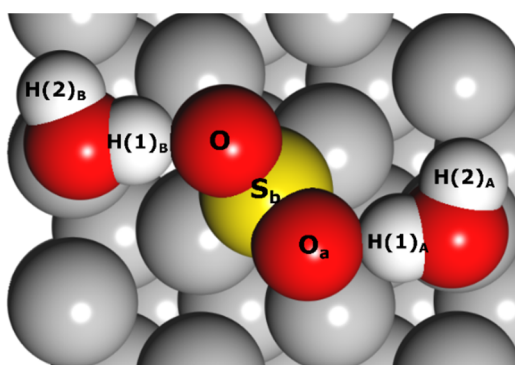


Figure 4.28: Atom positions in $\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}$ co-adsorption arrangement 10

Table 4.31: Bader Charge analysis of the SO_{2(ad)} + 2H₂O_(ad) co-adsorption system

Species	Atom	BC in single adsorbed molecule	BC in PtSO _{2(ad)} + 2H ₂ O _(ad)	$\Delta BC = (PtXY - PtX)$
SO ₂	S _b	4.01	4.01	0.00
	O	7.36	7.20	-0.16
	O _a	7.12	7.21	+0.09
H ₂ O(A)	H(1)	0.33	0.32	-0.01
	H(2)	0.36	0.38	+0.02
	O _a	7.22	7.18	-0.04
H ₂ O(B)	H(1)	0.33	0.32	-0.01
	H(2)	0.36	0.36	0.00
	O _a	7.22	7.20	-0.02

In the event where SO₂ was co-adsorbed with two H₂O molecules, a significantly weaker electronic interaction occurred between Pt(111) and all of the adsorbed species. If the BC of the co-adsorbed system is compared to the single adsorbed systems discussed in §4.4.2 and §4.9.2, an even greater depletion in electron density is observed for both H₂O. It is noted further that the BC difference in the H₂O positioned near the free O of SO₂, i.e. H₂O(B) in Figure 4.28, corresponds to a decrease in charge density. The decrease in charge density upon H₂O is indicative of a weakened electronic interaction between Pt(111) and H₂O, and that the observed increase in adsorption energy of H₂O when co-adsorbed SO₂ is present may be ascribed to an electronic interaction between SO₂ and H₂O.

4.11 SO₂ oxidation on Pt(111)

Since a comprehensive description of the adsorption properties of various sulphur oxides, as well as properties of SO₂ and H₂O in addition to H₂SO₄ and H₂ co-adsorption systems have been obtained, the oxidation energies of SO₂ on Pt(111) could now be determined.

4.11.1 Oxidation energy of adsorbed SO₂ on Pt(111)

Thus far, the adsorption of SO₂ and H₂O, as well as co-adsorption of the two species, were discussed. Similarly, the adsorption of H₂SO₄ and H₂ on Pt(111) were presented as well. From these results, the oxidation of SO₂ on Pt(111) leading to the formation of adsorbed H₂SO₄ and H₂ can now be discussed wherein the reactions of SO_{2(ad)} with H₂O_(ad) and SO_{2(ad)} with H₂O_(g) are compared. For each of the reactions above (i.e. 4.1 - 4.13), the most stable adsorption geometries (with energies) of each of the adsorbate molecules are summarised in Table 4.32.

Table 4.32: Adsorption energies of the most stable adsorption geometries of various molecules on pristine Pt(111)

Molecule	Adsorption geometry	$E_{free-ads}$ (eV)	Figure
SO ₂	FCC- η^2 -S _b ,O _a	-1.752	Figure 4.6a
SO	FCC- η^1 -S _f	-3.370	Figure 4.10
SO ₃	FCC- η^3 -S _a ,O _a ,O _a	+6.417	Figure 4.12
cis-H ₂ SO ₄	FCC- η^2 -H _a ,H _a -S _b	-0.921	Figure 4.14
trans-H ₂ SO ₄	FCC- η^3 -H _a ,O _a ,O _a -S _f	-0.753	Figure 4.14
H ₂ SO ₃	FCC- η^3 -H _a ,O _a ,O _a -S _f	-1.069	Figure 4.16
HSO ₄ ⁻	FCCHCP- η^3 -H _a ,O _a ,O _a	+3.652	Figure 4.17
H ₂ O	η^1 -O _a	-0.487	Figure 4.19
H ₂	η^1 -H _a	-0.107	Figure 4.19
H ₃ O ⁺	FCC- η^3 -H _a ,H _a ,H _a	-8.292	Figure 4.19
O ₂	η^2 -O _a ,O _a	-0.865	Figure 4.19

Similarly, the energies of the most stable co-adsorption arrangements are summarised as:

Table 4.33: Energies of the most stable co-adsorption arrangements on pristine Pt(111)

Molecule	E_{free} (eV)	Figure
SO ₂ + H ₂ O	-442.004	Figure 4.22h
SO ₂ + 2H ₂ O	-456.993	Figure 4.23j
2SO ₂	-445.790	Figure 4.21e
2SO ₂ + H ₂ O	-460.884	Figure 4.25e
cis-H ₂ SO ₄ + H ₂	-455.171	Figure 4.27g

From the above, in addition to the energies that have been obtained so far in this chapter, both the SO₂ oxidation energy as well as its mechanism on Pt(111) could now be evaluated.

4.11.2 The SO₂ oxidation mechanism on Pt(111)

Recall from Chapter 1, that the aim of this study is the development of a comprehensive description of the SO₂ oxidation mechanism on Pt. From the energies of the adsorption systems and single molecules presented above, it is now possible to describe several of the reactions introduced in §4.3, both for the Eley-Rideal as well as for the Langmuir-Hinshelwood mechanisms.

The total oxidation reaction energies of FCC-S_b,O_a adsorbed SO₂ on Pt(111) via an Eley-Rideal mechanism for the HyS reaction (4.1), excluding any intermediate steps as well as the exclusion (4.1 - 4.2) and inclusion (4.3 - 4.5) of intermediate reaction products, e.g. H₂SO₃, are:

	Reaction		ΔE_{free} (eV)
4.1	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{g})}$ +1.346
4.2	$2\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})} + \text{O}_{2(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_2\text{SO}_{4(\text{g})}$ -1.449
4.3	$\text{SO}_{3(\text{ad})} + \text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})}$ -8.177
4.4	$\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{3(\text{ad})}$ +0.628
4.5a	$\text{H}_2\text{SO}_{3(\text{ad})} + \text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$ -0.319
4.5b	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{g})}$ +1.037

It should be noted that in the Eley-Rideal mechanism one reactant is adsorbed and the other reacts directly from the gas-phase, whereas in the Langmuir-Hinshelwood mechanism both reactants are firstly adsorbed before a reaction occurs. The Eley-Rideal mechanism will therefore consist of fewer steps (two in this case) than the Langmuir-Hinshelwood mechanism (four steps), with different energies for each intermediate step. The oxidation energies via the Eley-Rideal (reactions 4.1a-b) and Langmuir-Hinshelwood mechanisms (reactions 4.1c-f) of FCC- η^2 -S_bO_a adsorbed SO₂ on Pt(111), including the possible intermediate adsorption steps for the HyS reaction (4.1), are:

	Reaction		ΔE_{free} (eV)
4.1a	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$ +0.309
4.1b	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{g})}$ +1.037
Nett	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{g})}$ +1.346
4.1c	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})} + \text{H}_2\text{O}_{(\text{g})}$ -0.743
4.1d	$\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})} + \text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}$ -0.770
4.1e	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{ad})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$ +1.822
4.1f	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{ad})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{g})}$ +1.037
Nett	$\text{SO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$	$\rightarrow$	$\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_{2(\text{g})}$ +1.346

The oxidation mechanisms above, i.e. Eley-Rideal (4.1a-b) and Langmuir-Hinshelwood (4.1c-f), are graphically compared in Figure 4.29.

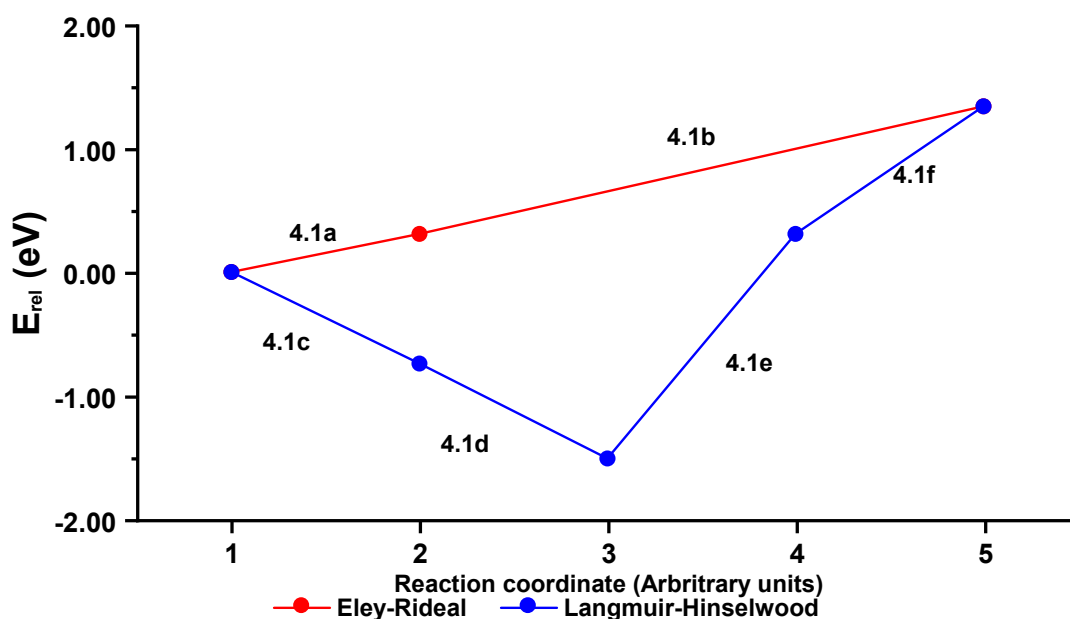


Figure 4.29: Energy-profile^a of the Eley-Rideal (red) and Langmuir-Hinshelwood (blue) mechanisms for the HyS reaction $\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2$ on pristine Pt(111); ^aNote that the energy is measured relative to the total energy of the reactants i.e. $\text{PtSO}_{2(\text{ad})} + 2\text{H}_2\text{O}_{(\text{g})}$.

Recall from §4.3.2 that the oxidation energy of the required HyS reaction (4.1) in the absence of Pt (i.e. in the gas phase), was +0.417 eV (Table 4.7). However, in the presence of Pt(111) (Figure 4.29), the required energy for the HyS reaction to occur via the Eley-Rideal mechanism (4.1a-b), leading to the initial formation of co-adsorbed H_2SO_4 and H_2 , was decreased to +0.309 eV. Nonetheless, a further 1.037 eV is required for the selective desorption of H_2 from the Pt(111). It should be noted further that the reaction energies described above are not alone sufficient to completely conclude the pathway of the HyS cycle. To improve the description of the reaction from the products in reactions 4.1a and 4.1b a transition-state analysis is required. Nevertheless, a starting point for future evaluation of the mechanism of the HyS cycle has been obtained through the results discussed above.

Two of the reaction steps in the Langmuir-Hinshelwood reaction, i.e. 4.1c and 4.1d, were exergonic ($\Delta E_{\text{free}} < 0$) whereas all of the steps in the Eley-Rideal mechanism were endergonic ($\Delta E_{\text{free}} > 0$). However, the required energy for the reaction step wherein adsorbed H_2SO_4 and adsorbed H_2 are formed (in Langmuir-Hinshelwood), was significantly higher than the last step of the Eley-Rideal mechanism. Therefore, in terms of energy, the SO_2 oxidation on pristine Pt(111) via the Eley-Rideal mechanism was favoured above the Langmuir-Hinshelwood mechanism.

In §4.3.2, it was noted further that SO_2 , similar to its gas phase reactions, can undergo various other reactions in addition to the HyS reaction when adsorbed on Pt(111). Among the reactions presented in §4.3.2, reactions 4.1 - 4.9 and 4.11 are of significant interest, since it directly involves

either SO₂ or H₂SO₄. Furthermore, the self-reaction between two co-adsorbed SO₂ is of interest as well, since SO₃ and SO are both formed with different reactivities towards H₂O. From the energies that have been obtained thus far, the energies of SO₂ self-oxidation as well as the oxidation with H₂O (reactions 4.3 - 4.5) on Pt(111), can be described as follows:

	Reaction		ΔE_{free} (eV)
	2SO _{2(ad)}	→	SO _{3(g)} + SO _(ad) +1.893
	2SO _{2(ad)}	→	SO _{3(ad)} + SO _(g) +13.035
	SO _{2(ad)} +SO _{2(g)}	→	SO _{3(g)} + SO _(ad) +0.113
4.3	SO _{3(ad)} + H ₂ O _(g)	→	H ₂ SO _{4(ad)} -8.177
4.4	SO _{2(ad)} + H ₂ O _(ad)	→	H ₂ SO _{3(ad)} +0.628
4.5	H ₂ SO _{3(ad)} + H ₂ O _(g)	→	H ₂ SO _{4(ad)} + H _{2(ad)} -0.319
	SO _(ad) + H ₂ O _(g)	→	SO _{2(ad)} + H _{2(ad)} +1.241

The redox reaction between two SO₂ molecules appears to favour, similar to the reaction between SO₂ and H₂O, the Eley-Rideal mechanism and leads to the formation of adsorbed SO_(ad) and desorbed SO_{3(g)}. In the event where a reaction between two co-adsorbed SO₂ molecules on Pt(111) does occur (i.e. Langmuir-Hinshelwood), the possibility for the formation of co-adsorbed SO₃ and SO does exist. However, a significantly greater amount of energy is required for the Langmuir-Hinshelwood redox mechanism between two co-adsorbed SO₂ molecules. It is noted further that SO₃ desorption, despite being endergonic, is more likely to occur than desorption of SO. It is possible, however, that an adsorbed or desorbing SO₃ might react with near-positioned H₂O_(g), leading to the formation of adsorbed H₂SO₄ (4.3). However, despite having a lower probability, the formation of adsorbed SO_{2(ad)} and desorbing H_{2(g)} could also result from an endergonic reaction between adsorbed SO_(ad) and gaseous H₂O_(g). A greater amount of energy is required for the formation of H₂SO_{3(ad)} as an intermediate product from the reaction between co-adsorbed SO₂ and H₂O, whereafter H₂SO₃ subsequently reacts with a second surrounding H₂O_(g) leading to the formation of H₂SO_{4(ad)} and H_{2(ad)}.

Based upon the reaction energies between co-adsorbed SO₂ and H₂O, in the less probable event of the Langmuir-Hinshelwood mechanism, as well as the self-oxidation-reduction between two co-adsorbed SO₂, the probability that adsorbed SO₂ is directly oxidised by two H₂O to form H₂SO₄ and H₂ is higher than the redox-reaction between two co-adsorbed SO₂.

4.12 Conclusion

In this chapter it was observed that SO_2 is adsorbed stronger than H_2O on $\text{Pt}(111)$ and furthermore that the adsorption of H_2O is significantly influenced, both energetically as well as charge related, by the presence of co-adsorbed SO_2 . In contrast, SO_2 does not seem to be affected to such a significant extent by co-adsorbed H_2O . Therefore, the energetic properties and behaviour of SO_2 and H_2O on the Pt surface are highly dependent upon the specific order wherein the adsorption of different molecules occur. From a stereochemical perspective, various structural changes, such as bond elongation and bond angle distortion, within SO_2 , H_2O as well as H_2SO_4 , were identified to occur upon the adsorption on $\text{Pt}(111)$.

Further Bader Charge analysis of both single adsorbed (e.g. $\text{SO}_{2(\text{ad})}$), as well as co-adsorption systems (e.g. $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$) have proposed that the electronic interaction between SO_2 and Pt is stronger than between H_2O and Pt. In addition, the Bader analysis have confirmed that the adsorption of SO_2 on $\text{Pt}(111)$ significantly depletes the charge-density of the surface and subsequently weakens the interaction between Pt and H_2O .

With respect to the development of an oxidation mechanism of SO_2 , some clarity regarding the formation of H_2SO_4 on the surface was obtained as well. In this chapter it was further observed that both the cis- and trans-isomers of H_2SO_4 are spontaneously adsorbed on $\text{Pt}(111)$, and that the adsorption energies of both H_2SO_4 isomers are not as highly exergonic as that of SO_2 adsorption. Nonetheless, despite still requiring energy, the oxidation of SO_2 with H_2O to form H_2SO_4 and H_2 is significantly enhanced through the employment of $\text{Pt}(111)$ as the catalyst.

It is noted further that progress regarding the energetics of SO_2 and H_2O co-adsorption as well as the oxidation to form H_2SO_4 and H_2 was made. However, although significant insight towards the co-adsorption behaviour of SO_2 and H_2O was obtained, the oxidation of SO_2 by H_2O from the most favoured adsorption arrangement may require adsorbate migration on the surface before the longed products are formed. Nevertheless, an Eley-Rideal mechanism does seem to be favoured in the reaction between SO_2 and H_2O on pristine $\text{Pt}(111)$. Once these remaining uncertainties are clarified, a more comprehensive description of the Eley-Rideal and Langmuir-Hinshelwood SO_2 oxidation mechanisms on $\text{Pt}(111)$ may be obtained.

In this chapter, single molecule adsorption of various gas molecules, as well as the co-adsorption of SO_2 and H_2O on $\text{Pt}(111)$, have been discussed. The adsorption energies and other properties, such as Bader charges of various SO_2 related compounds as single adsorbed systems, were discussed and compared. As these properties were consequently identified, the next step that may be taken to describe the oxidation of SO_2 more thoroughly is to apply statistical mechanics

to identify the influence of temperature on the oxidation behaviour of SO_2 since this study only presented the fundamental investigation of $\text{SO}_{2(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption and the subsequent oxidation of adsorbed SO_2 on Pt(111).

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In Chapters 1 and 2 it was seen that the HyS cycle might serve as a viable means for the production of hydrogen (H_2) in electrolyzers, but that SO_2 poisoning of the Pt electrode and its subsequent selectivity and sensitivity reduction are still matters of concern. In Chapters 1 and 2, it was further concluded that a fundamental understanding of the adsorption behaviour of SO_2 and H_2O on Pt is still required as a first step towards the improvement of Pt catalyst performance. Molecular modelling, and in particular density functional theory (DFT), was further identified as a viable means to investigate hetero catalytic processes such as adsorption in the HyS cycle. Thereafter, the precise mathematical model, as well as specific mathematical parameters employed in this DFT investigation, were discussed further in Chapter 3.

In Chapter 4 it was reiterated that SO_2 is adsorbed relatively strongly on pristine Pt(111) in comparison to H_2O . It was also noted that the adsorption energy of H_2O on Pt(111) is significantly influenced by the presence (or absence) of adsorbed SO_2 with a relative H_2O adsorption energy increase of ~52% when pre-adsorbed SO_2 is indeed present. In contrast, however, it does not seem that the adsorption of SO_2 on Pt(111) is as significantly influenced, both in terms of adsorption geometry and adsorption energy (with a relative SO_2 adsorption energy increase of ~12%), by the presence of pre-adsorbed H_2O . In terms of stereochemical properties several structural changes were observed, both in SO_2 as well as H_2O upon their adsorption on Pt(111) and both displayed, in particular, a dependency on the presence of co-adsorbed species. In addition to differences in adsorption energy between single and co-adsorbed systems, the relative magnitudes of the structural changes (e.g. bond lengths and bond angles) observed in H_2O when co-adsorption occurs, are greater than the changes observed in SO_2 . The findings in Chapter 4 have further confirmed observations made in earlier work by Ungerer et. al.[13,14].

In addition to the single and co-adsorption properties of SO_2 and H_2O , the adsorption properties of sulphuric acid (H_2SO_4) on pristine Pt(111) display preference towards the direct formation of H_2SO_4 when SO_2 oxidation with H_2O occurs. From the comparison of cis- H_2SO_4 with trans- H_2SO_4 adsorption it can be seen that the former isomer tends to be adsorbed stronger on Pt(111) and that the formation of the cis- rather than the trans-isomer as adsorbed oxidation product is energetically favoured. It was noted that H_2 and H_2O are, in comparison to both SO_2 and H_2SO_4 , adsorbed comparatively weakly on Pt(111). In order for the SO_2 oxidation to occur readily on Pt(111) however, it is noted that H_2O migration from its most stable adsorption location in the $SO_{2(ad)} + 2H_{2O(ad)}$ co-adsorption arrangement on Pt(111), is required. The possible necessity of

H₂O molecule migration on Pt(111) for the occurrence of SO₂ oxidation could, however, be clarified further by means of transition-state analysis.

Regarding the charge distribution of adsorbed molecules, Bader charge analysis of various SO₂ and H₂O co-adsorption systems have provided further insight into the interaction between the Pt surface, SO₂ and H₂O [145,146]. A stronger electronic Pt-adsorbate interaction, characterised by a greater BC difference, is observed in SO₂ adsorption systems than in the H₂O adsorption systems. In addition, Bader analyses of SO₂ + H₂O and SO₂ + 2H₂O co-adsorption systems have provided further insight regarding the charge distribution effects of adsorbed SO₂ on the electron donation ability of Pt, and its subsequent influence on the Pt-H₂O interaction. A notably weaker electronic interaction between Pt and H₂O is observed in the presence of co-adsorbed SO₂. In contrast, however, it was shown that the charge interaction between Pt and adsorbed SO₂ is not as significantly influenced by the presence of co-adsorbed H₂O. Since the electronic interaction between Pt and H₂O forms an essential step in the HyS cycle, the detrimental influence of adsorbed SO₂ on the Pt electrode becomes evident.

Insight into the adsorption behaviour of both H₂SO₄ isomers on Pt(111) was obtained as well, with the cis-isomer displaying stronger adsorption on Pt(111) in comparison to the trans-isomer. Furthermore, the stronger adsorption of cis-H₂SO₄ than trans-H₂SO₄ may in part be ascribed to the relative stabilities of the isomers. Since trans-H₂SO₄ is lower in energy than cis-H₂SO₄ adsorption of the trans-isomer will not occur as strongly as adsorption of cis-H₂SO₄. Furthermore, the specific isomer structure (stereochemistry) can be a further ascription. In trans-H₂SO₄ only one H atom is able to be adsorbed in the preferred atop position on Pt(111). However, in cis-H₂SO₄ both H atoms are able to simultaneously interact with Pt atoms in the favoured atop position, i.e. electron donation from Pt to both H occur consequently stabilising the FCC- η^2 -H_a,H_a adsorption geometry.

In Chapter 4 it was seen as well that despite containing two steps with significantly favourable reaction energies, the formation-step of adsorbed H₂SO₄ and H₂ in the Langmuir-Hinshelwood reaction is significantly higher than the Eley-Rideal mechanism. As a result, based on the findings obtained in this study, the occurrence of the Eley-Rideal SO₂ oxidation mechanism is likely to be favoured on Pt(111).

5.2 Recommendations regarding Future Research

In this dissertation, only SO_{2(ad)} + H₂O_(ad) co-adsorption arrangements consisting of three or fewer adsorbate molecules were discussed, with the aim to better understand the fundamental properties of SO₂ adsorption on Pt. The findings of this study can thus be elaborated further by

investigating surface-coverage effects of adsorbed SO_2 and H_2O in larger systems on the adsorption as well as on the SO_2 oxidation mechanism. Moreover, solvation effects of H_2O on adsorbed SO_2 , in comparison to the absence of the Pt catalyst, can be a topic of further investigation.

In this study a generalised gradient approximation with the Perdew-Burke-Erznherhoff (PBE) functional was employed. However, the PBE functional is not necessarily the only functional that may be employed to investigate the SO_2 - H_2O -interaction on Pt(111). Thus, for further elaboration, it might be considered to investigate this interaction by utilising other functionals such as the Perdew-Wang-91 (PW91) [66,156].

The dissociation of H_2SO_4 on Pt, as well as the formation of intermediate oxidation products such as H_2SO_3 , SO_3 and SO_4 , may in future be another topic of investigation. In addition, the density of state analyses of sulphur oxide adsorption systems on Pt(111) is a further means to improve the description of SO_2 adsorption properties on Pt catalysts. Furthermore, only Pt(111) was discussed in this study. The co-adsorption of SO_2 and H_2O on other Pt Miller surfaces, such as Pt(100) and Pt(001), may be of interest in future studies and compared to the findings for Pt(111) in this dissertation.

Since the co-adsorption behaviour of the stoichiometric co-adsorption of SO_2 and H_2O on Pt(111) (i.e. 1:2) was discussed, the next step in the investigation of SO_2 oxidation at the anode of the electrolyser, within the HyS cycle, is to evaluate the co-adsorption of H_2SO_4 and H_2 in Pt(111) as well. Once a comprehensive description of the co-adsorption properties of H_2SO_4 and H_2 is developed, co-adsorption of SO_2 with other related species such as SO_3 , H_3O^+ , SO and O_2 , may be performed in order to improve the stereochemical description of the HyS cycle [167].

The adsorption properties of some ionic sulphur oxides were discussed in Chapter 4, and it was noted that anionic sulphates are primarily adsorbed endergonically on Pt(111), i.e. $\Delta E_{\text{free}} > 0$. However, the analysis of H_3O^+ adsorption on Pt(111) does display a strong exergonic behaviour, indicating a substantial influence on Pt in the event where H_2SO_4 dissociation might occur. The precise behaviour, as well as the probability of H_2SO_4 dissociation on Pt(111), may in future be evaluated not only through the investigation of $\text{H}_2\text{SO}_{4(\text{ad})} + \text{H}_2\text{O}_{(\text{ad})}$ co-adsorption studies but also by accompanying it with adsorption studies of $\text{HSO}_{4(\text{ad})}^- + \text{H}_3\text{O}_{(\text{ad})}^+$ co-adsorption systems.

It is further noted that H_2SO_4 and H_2 , despite being the primary products of the HyS cycle, are not necessarily the only reaction products that might form on Pt(111) and that several intermediate and by-products may possibly be formed as well. Among other proposed oxidation products that might be formed are SO_4 , $\text{S}_2\text{O}_4^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ [3].

Various uncertainties regarding the Langmuir-Hinshelwood and Eley-Rideal mechanisms in the HyS cycle were clarified. In Chapter 4, it was noted that, based purely upon the energies of the reactants and products in the SO_2 oxidation reaction, the Eley-Rideal mechanism is the probable dominant pathway. An important factor that may significantly influence the mechanism preference, however, is the formation of transition-states and may be a popular topic for further investigation into SO_2 oxidation on Pt catalysts. In addition, the description of the energetics of SO_2 oxidation on Pt catalysts may be enhanced further through frequency analysis and zero-point energy determination.

The identification of other possible catalysts for the HyS cycle may be of interest in future research as well, wherein the adsorption and oxidation properties of SO_2 and H_2O on bi- or trimetallic alloy catalysts, e.g. Pt-Pd and Pt-Ni₂, can be compared to that of the pristine Pt(111) catalyst presented in this study. In addition, other monometallic catalysts, such as Pd and Ni, can be topics of investigation and compared to Pt in terms of suitability for the HyS cycle. Moreover, in addition to the investigation of alloy catalysts, the influence of different substrate support layers, such as graphene or glassy carbon, on the reactivity and selectivity of thin-film Pt catalysts in the HyS cycle, may be a topic of further investigation.

Given the proposed topics for possible further investigation, the results presented in this dissertation may, in future, serve as a reference standard in the analysis of alloy catalyst performance in the HyS cycle.

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CHAPTER 6 APPENDIX

6.1 Pt(111) POSCAR file

Atom coordinates are defined in the POSCAR file and expressed in direct coordinates, i.e. the atom coordinates are expressed as a fractional quantity of the cell size. The direct coordinates are transformable, through matrix multiplication, to be expressed as Cartesian coordinates as follows:

Recall from linear algebra that three vectors $\vec{a}_1 = \langle a_{11}, a_{12}, a_{13} \rangle$, $\vec{a}_2 = \langle a_{21}, a_{22}, a_{23} \rangle$ and $\vec{a}_3 = \langle a_{31}, a_{32}, a_{33} \rangle$ are representable in the form of a (3 x 3) matrix A as such that:

$$A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

Let it be assumed that the unit cell dimensions (i.e. defined by the 3 vector matrix A above) are:

11.0868974992	0.0000000000	0.0000000000
5.5434487496	9.6015348835	0.0000000000
0.0000000000	0.0000000000	23.0524139012

and that the atom positions of a random diatomic molecular system X_2 in the unit cell are expressed in direct coordinates, i.e. the two-vector matrix $\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ b_{21} & b_{22} & b_{23} \end{bmatrix}$ as:

0.5666666667	0.6666666667	0.4500000000
0.4166666667	0.6166666667	0.5000000000

After matrix multiplication, expressed in Cartesian coordinates the positions of the atoms are therefore expressed as the (2 x 3) matrix:

9.9782077498	6.4010232560	10.3735862555
8.0380006875	5.9209465118	11.5262069506

6.2 Stackgen and Metadise

The input file for the assembling of the bottom 32 Pt atoms in the bulk structure is:

```
TITLE
Pt bulk structure Fm -3m
ICSD -241737
ENDS
print vasp 1
VASP
Pt
1.0
+7.8396204040      +0.0000000000      +0.0000000000
+0.0000000000      +7.8396204040      +0.0000000000
+0.0000000000      +0.0000000000      +7.8396204040
Pt
32
Selective
Cartesian
+0.0000000000      +0.0000000000      +0.0000000000      T      T      T
+0.0000000000      +1.9599051010      +1.9599051010      T      T      T
+1.9599051010      +0.0000000000      +1.9599051010      T      T      T
+1.9599051010      +1.9599051010      +0.0000000000      T      T      T
+0.0000000000      +0.0000000000      +3.9198102020      T      T      T
+0.0000000000      +1.9599051010      +5.8797153030      T      T      T
+1.9599051010      +0.0000000000      +5.8797153030      T      T      T
+1.9599051010      +1.9599051010      +3.9198102020      T      T      T
+0.0000000000      +3.9198102020      +0.0000000000      T      T      T
+0.0000000000      +5.8797153030      +1.9599051010      T      T      T
+1.9599051010      +3.9198102020      +1.9599051010      T      T      T
+1.9599051010      +5.8797153030      +0.0000000000      T      T      T
+0.0000000000      +3.9198102020      +3.9198102020      T      T      T
+0.0000000000      +5.8797153030      +5.8797153030      T      T      T
+1.9599051010      +3.9198102020      +5.8797153030      T      T      T
+1.9599051010      +5.8797153030      +3.9198102020      T      T      T
+3.9198102020      +0.0000000000      +0.0000000000      T      T      T
+3.9198102020      +1.9599051010      +1.9599051010      T      T      T
+5.8797153030      +0.0000000000      +1.9599051010      T      T      T
+5.8797153030      +1.9599051010      +0.0000000000      T      T      T
+3.9198102020      +0.0000000000      +3.9198102020      T      T      T
+3.9198102020      +1.9599051010      +5.8797153030      T      T      T
+5.8797153030      +0.0000000000      +5.8797153030      T      T      T
+5.8797153030      +1.9599051010      +3.9198102020      T      T      T
+3.9198102020      +3.9198102020      +0.0000000000      T      T      T
+3.9198102020      +5.8797153030      +1.9599051010      T      T      T
+5.8797153030      +3.9198102020      +1.9599051010      T      T      T
+5.8797153030      +5.8797153030      +0.0000000000      T      T      T
+3.9198102020      +3.9198102020      +3.9198102020      T      T      T
+3.9198102020      +5.8797153030      +5.8797153030      T      T      T
+5.8797153030      +3.9198102020      +5.8797153030      T      T      T
+5.8797153030      +5.8797153030      +3.9198102020      T      T      T
ENDS
POTE
SPEC
Pt 0.00 195.084
ENDS
ENDS
SURFACE
MILLER 1 1 1
START
STACKGEN SYSTEMATIC
START
STOP
```

The **input.txt** file used in the assembling of the top half of the Pt(111) Miller plane is as follows:

```

TITLE
Pt bulk structure Fm -3m
ICSD -241737
ENDS
print vasp 1
VASP
Pt
1.0
+7.8396204040      +0.0000000000      +0.0000000000
+0.0000000000      +7.8396204040      +0.0000000000
+0.0000000000      +0.0000000000      +7.8396204040
Pt
32
Selective
Cartesian
+0.0000000000      +0.0000000000      +0.0000000000      T      T      T
+0.0000000000      +1.9599051010      +1.9599051010      T      T      T
+1.9599051010      +0.0000000000      +1.9599051010      T      T      T
+1.9599051010      +1.9599051010      +0.0000000000      T      T      T
+0.0000000000      +0.0000000000      +3.9198102020      T      T      T
+0.0000000000      +1.9599051010      +5.8797153030      T      T      T
+1.9599051010      +0.0000000000      +5.8797153030      T      T      T
+1.9599051010      +1.9599051010      +3.9198102020      T      T      T
+0.0000000000      +3.9198102020      +0.0000000000      T      T      T
+0.0000000000      +5.8797153030      +1.9599051010      T      T      T
+1.9599051010      +3.9198102020      +1.9599051010      T      T      T
+1.9599051010      +5.8797153030      +0.0000000000      T      T      T
+0.0000000000      +3.9198102020      +3.9198102020      T      T      T
+0.0000000000      +5.8797153030      +5.8797153030      T      T      T
+1.9599051010      +3.9198102020      +5.8797153030      T      T      T
+1.9599051010      +5.8797153030      +3.9198102020      T      T      T
+3.9198102020      +0.0000000000      +0.0000000000      T      T      T
+3.9198102020      +1.9599051010      +1.9599051010      T      T      T
+5.8797153030      +0.0000000000      +1.9599051010      T      T      T
+5.8797153030      +1.9599051010      +0.0000000000      T      T      T
+3.9198102020      +0.0000000000      +3.9198102020      T      T      T
+3.9198102020      +1.9599051010      +5.8797153030      T      T      T
+5.8797153030      +0.0000000000      +5.8797153030      T      T      T
+5.8797153030      +1.9599051010      +3.9198102020      T      T      T
+3.9198102020      +3.9198102020      +0.0000000000      T      T      T
+3.9198102020      +5.8797153030      +1.9599051010      T      T      T
+5.8797153030      +3.9198102020      +1.9599051010      T      T      T
+5.8797153030      +5.8797153030      +0.0000000000      T      T      T
+3.9198102020      +3.9198102020      +3.9198102020      T      T      T
+3.9198102020      +5.8797153030      +5.8797153030      T      T      T
+5.8797153030      +3.9198102020      +5.8797153030      T      T      T
+5.8797153030      +5.8797153030      +3.9198102020      T      T      T
ENDS
POTE
SPEC
Pt 0.00 195.084
ENDS
ENDS
SURFACE
MILLER 1 1 1
START
STACKGEN 1
START
STOP

```

The **sum_o0001.out** file used to identify the location of mirror planes is:

```
#Miller      1      1      1
d spacing =  4.5262069505938882
lattice energy = 0.0000000000000000 eV, area = 106.45123308780749
list code    dipole    slice energy    attachment energy    /atom surf en
code 1  =    0.000000000.00000    0.00000    -0.00000    mirror
code 2  =    0.000000000.00000    0.00000    -0.00000
code 3  =    0.000000000.00000    0.00000    -0.00000
code 4  =    0.000000000.00000    0.00000    -0.00000
code 5  =    0.000000000.00000    0.00000    -0.00000
code 6  =    0.000000000.00000    0.00000    -0.00000
code 7  =    0.000000000.00000    0.00000    -0.00000
code 8  =    0.000000000.00000    0.00000    -0.00000
code 9  =    0.000000000.00000    0.00000    -0.00000    mirror
code 10 =    0.000000000.00000    0.00000    -0.00000
code 11 =    0.000000000.00000    0.00000    -0.00000
code 12 =    0.000000000.00000    0.00000    -0.00000
code 13 =    0.000000000.00000    0.00000    -0.00000
code 14 =    0.000000000.00000    0.00000    -0.00000
code 15 =    0.000000000.00000    0.00000    -0.00000
code 16 =    0.000000000.00000    0.00000    -0.00000
code 17 =    0.000000000.00000    0.00000    -0.00000    mirror
code 18 =    0.000000000.00000    0.00000    -0.00000
code 19 =    0.000000000.00000    0.00000    -0.00000
code 20 =    0.000000000.00000    0.00000    -0.00000
code 21 =    0.000000000.00000    0.00000    -0.00000
code 22 =    0.000000000.00000    0.00000    -0.00000
code 23 =    0.000000000.00000    0.00000    -0.00000
code 24 =    0.000000000.00000    0.00000    -0.00000
code 25 =    0.000000000.00000    0.00000    -0.00000    mirror
code 26 =    0.000000000.00000    0.00000    -0.00000
code 27 =    0.000000000.00000    0.00000    -0.00000
code 28 =    0.000000000.00000    0.00000    -0.00000
code 29 =    0.000000000.00000    0.00000    -0.00000
code 30 =    0.000000000.00000    0.00000    -0.00000
code 31 =    0.000000000.00000    0.00000    -0.00000
code 32 =    0.000000000.00000    0.00000    -0.00000
```

6.3 POSCAR and CONTCAR files

Below is the POSCAR file of the assembled FCC-S_bO_a SO_{2(ad)} adsorption system before optimisation. Note that selective dynamics constrain the movement of atoms in the system and allows for the addition of the FFF and TTT option that defines if the atom is allowed to move in the x-, y- and z directions during the optimisation step, i.e. TTT to allow movement or FFF to constrain and atom to its initial position.

6.3.1 Optimisation POSCAR input file

```
PtSO
1.0
11.0868974992 0.0000000000 0.0000000000
 5.5434487496 9.6015348835 0.0000000000
 0.0000000000 0.0000000000 23.0524139012
Pt O S
64 2 1
Selective Dynamics
Direct
0.6666666667 0.6666666667 0.0000000000 F F F
0.4166666667 0.9166666667 0.0000000000 F F F
0.4166666667 0.6666666667 0.0000000000 F F F
0.1666666667 0.9166666667 0.0000000000 F F F
0.9166666667 0.4166666667 0.0000000000 F F F
0.9166666667 0.1666666667 0.0000000000 F F F
0.6666666667 0.4166666667 0.0000000000 F F F
0.1666666667 0.1666666667 0.0000000000 F F F
0.9166666667 0.9166666667 0.0000000000 F F F
0.9166666667 0.6666666667 0.0000000000 F F F
0.6666666667 0.9166666667 0.0000000000 F F F
0.1666666667 0.6666666667 0.0000000000 F F F
0.6666666667 0.1666666667 0.0000000000 F F F
0.4166666667 0.4166666667 0.0000000000 F F F
0.4166666667 0.1666666667 0.0000000000 F F F
0.1666666667 0.4166666667 0.0000000000 F F F
0.7500000000 0.7500000000 0.0981720823 F F F
0.7500000000 0.5000000000 0.0981720823 F F F
0.5000000000 0.7500000000 0.0981720823 F F F
0.0000000000 0.5000000000 0.0981720823 F F F
0.5000000000 0.0000000000 0.0981720823 F F F
0.2500000000 0.2500000000 0.0981720823 F F F
0.2500000000 0.0000000000 0.0981720823 F F F
1.0000000000 0.2500000000 0.0981720823 F F F
0.5000000000 0.5000000000 0.0981720823 F F F
0.2500000000 0.7500000000 0.0981720823 F F F
0.2500000000 0.5000000000 0.0981720823 F F F
0.0000000000 0.7500000000 0.0981720823 F F F
0.7500000000 0.2500000000 0.0981720823 F F F
0.7500000000 0.0000000000 0.0981720823 F F F
0.5000000000 0.2500000000 0.0981720823 F F F
0.0000000000 0.0000000000 0.0981720823 F F F
0.3333333333 0.3333333333 0.1961890898 T T T
0.0833333333 0.5833333333 0.1961890898 T T T
0.0833333333 0.3333333333 0.1961890898 T T T
0.8333333333 0.5833333333 0.1961890898 T T T
0.5833333333 0.0833333333 0.1961890898 T T T
0.5833333333 0.8333333333 0.1961890898 T T T
0.3333333333 0.0833333333 0.1961890898 T T T
0.8333333333 0.8333333333 0.1961890898 T T T
0.5833333333 0.5833333333 0.1961890898 T T T
0.5833333333 0.3333333333 0.1961890898 T T T
0.3333333333 0.5833333333 0.1961890898 T T T
0.8333333333 0.3333333333 0.1961890898 T T T
0.3333333333 0.8333333333 0.1961890898 T T T
0.0833333333 0.0833333333 0.1961890898 T T T
0.0833333333 0.8333333333 0.1961890898 T T T
0.8333333333 0.0833333333 0.1961890898 T T T
0.4166666667 0.4166666667 0.2959983392 T T T
0.4166666667 0.1666666667 0.2959983392 T T T
0.1666666667 0.4166666667 0.2959983392 T T T
0.6666666667 0.1666666667 0.2959983392 T T T
0.1666666667 0.6666666667 0.2959983392 T T T
0.9166666667 0.9166666667 0.2959983392 T T T
0.9166666667 0.6666666667 0.2959983392 T T T
0.6666666667 0.9166666667 0.2959983392 T T T
0.1666666667 0.1666666667 0.2959983392 T T T
0.9166666667 0.4166666667 0.2959983392 T T T
0.9166666667 0.1666666667 0.2959983392 T T T
0.6666666667 0.4166666667 0.2959983392 T T T
0.4166666667 0.9166666667 0.2959983392 T T T
0.4166666667 0.6666666667 0.2959983392 T T T
0.1666666667 0.9166666667 0.2959983392 T T T
0.6666666667 0.6666666667 0.2959983392 T T T
0.5370376632 0.4134295084 0.4132411899 T T T
0.5005149264 0.6048403910 0.3834287504 T T T
0.5154546885 0.5205508965 0.3669537803 T T T
```

6.3.2 Optimisation CONTCAR output file

Pt O S

1.0

11.0868974992	0.0000000000	0.0000000000
5.5434487496	9.6015348835	0.0000000000
0.0000000000	0.0000000000	23.0524139012

Pt O S

64 2 1

Selective Dynamics

Direct

0.666666667	0.666666667	0.000000000	F	F	F
0.416666667	0.916666667	0.000000000	F	F	F
0.416666667	0.666666667	0.000000000	F	F	F
0.166666667	0.916666667	0.000000000	F	F	F
0.916666667	0.416666667	0.000000000	F	F	F
0.916666667	0.166666667	0.000000000	F	F	F
0.666666667	0.416666667	0.000000000	F	F	F
0.166666667	0.166666667	0.000000000	F	F	F
0.916666667	0.916666667	0.000000000	F	F	F
0.916666667	0.666666667	0.000000000	F	F	F
0.666666667	0.916666667	0.000000000	F	F	F
0.166666667	0.666666667	0.000000000	F	F	F
0.666666667	0.166666667	0.000000000	F	F	F
0.416666667	0.416666667	0.000000000	F	F	F
0.416666667	0.166666667	0.000000000	F	F	F
0.166666667	0.416666667	0.000000000	F	F	F
0.750000000	0.750000000	0.0981720823	F	F	F
0.750000000	0.500000000	0.0981720823	F	F	F
0.500000000	0.750000000	0.0981720823	F	F	F
0.000000000	0.500000000	0.0981720823	F	F	F
0.500000000	0.000000000	0.0981720823	F	F	F
0.250000000	0.250000000	0.0981720823	F	F	F
0.250000000	0.000000000	0.0981720823	F	F	F
1.000000000	0.250000000	0.0981720823	F	F	F
0.500000000	0.500000000	0.0981720823	F	F	F
0.250000000	0.750000000	0.0981720823	F	F	F
0.250000000	0.500000000	0.0981720823	F	F	F
0.000000000	0.750000000	0.0981720823	F	F	F
0.750000000	0.250000000	0.0981720823	F	F	F
0.750000000	0.000000000	0.0981720823	F	F	F
0.500000000	0.250000000	0.0981720823	F	F	F
0.000000000	0.000000000	0.0981720823	F	F	F
0.3339681113	0.3357723314	0.1977325765	T	T	T
0.0831503879	0.5832065643	0.1958752128	T	T	T
0.0819621903	0.3337141593	0.1958008961	T	T	T
0.8333637988	0.5837819241	0.1957512176	T	T	T
0.5818193839	0.0853219180	0.1960622022	T	T	T
0.5820678276	0.8353916394	0.1956571960	T	T	T
0.3314538539	0.0848221700	0.1956803715	T	T	T
0.8325316334	0.8345992076	0.1961682643	T	T	T
0.5825597431	0.5846483963	0.1967162001	T	T	T
0.5825287088	0.3359496410	0.1975838029	T	T	T
0.3333745493	0.5844871652	0.1969752032	T	T	T
0.8284061599	0.3365220117	0.1983992273	T	T	T
0.3334760388	0.8318563461	0.1976649355	T	T	T
0.0815544529	0.0849080091	0.1959740917	T	T	T
0.0821727688	0.8346668626	0.1957949825	T	T	T
0.8322718517	0.0847925546	0.1960308281	T	T	T
0.4067294065	0.4117065266	0.2969625666	T	T	T
0.4141715886	0.1645177140	0.2967416347	T	T	T
0.1601456902	0.4181203389	0.2965758934	T	T	T
0.6650362547	0.1673729156	0.2952505818	T	T	T
0.1615305524	0.6699563907	0.2944704015	T	T	T
0.9142853324	0.9197220107	0.2961663261	T	T	T
0.9148024778	0.6697409825	0.2960374754	T	T	T
0.6653548767	0.9194318258	0.2960771307	T	T	T
0.1635611866	0.1683547949	0.2965252256	T	T	T
0.9170919286	0.4186615721	0.2964393024	T	T	T
0.9146381192	0.1687072584	0.2966057238	T	T	T
0.6705621234	0.4185779128	0.3014130755	T	T	T
0.4141035806	0.9220085926	0.2958364620	T	T	T
0.4107512616	0.6778473535	0.2985927578	T	T	T
0.1624755105	0.9210115860	0.2959805036	T	T	T
0.6681746443	0.6725587385	0.2941908845	T	T	T
0.4430088002	0.4590096586	0.3903282533	T	T	T
0.5593259537	0.5896135524	0.4236861313	T	T	T
0.5187223737	0.5363651180	0.3745097743	T	T	T

6.4 Structure Optimisation (Relaxation) INCAR file

SYSTEM = Pt_SO2

Startparameter for this run:

```
##PREC = Accurate Def: normal, accurate (activate for SP and NMR calculations), single (STM calculations)
LASPH = T aspherical Exc in radial PAW
GGA = PE GGA type
##VOSKOWN = 1 Vosko Wilk Nusair interpolation (only for PW91)
ISPIN = 2 spin polarized calculation (1 for non spin polarized calculations)
##NUPDOWN = -1.0000 fix difference electrons up-down
## Pt
##MAGMOM = 1*0
##ICHARG = 1 how to construct the initial charge density, 1-file(activate if restarting
from non-spin polarised calculation) Def:2-atom 10-const

##LDAU = T
##LDAUTYPE = 2 Dudarev et al. approach
## O C H
##LDAUL = -1 -1 -1 no on-site: -1, p: 1, d: 2, f: 3
##LDAUU = 0.0 0.0 0.0 U values
##LDAUJ = 0.0 0.0 0.0 J values
LMAXMIX = 4 for the calculation of band structures p:2, d: 4, f: 6
Parallelization
##LPLANE = T activate data distribution (only activate if NGZ is at least 3*(# of
cores)/NPAR)
NCORE = 4 #NUMBER OF CORES PER ORBITAL
##NPAR = 4 NGZ=n*NPAR, NPAR=sqrt(cores) (do not use for NMR or FREQ
calculations)
##KPAR = 5 # of compute nodes or k-points (try to make them the same by
increasing compute nodes), whichever is the smallest, divide by 2 or 4 if problems
(N=#cores/KPAR) (do not use for SP calculations)
##NBANDS = # of bands (increase if necessary) (# of cores = NBANDS/8)
Dispersion Interaction
IVDW = 12 Van der Waals corrections - DFT-D3 method
##VDW_S6 = 0.75 Global scaling factor PBE: 0.75
Electronic Relaxation
ENCUT = 400.0 kinetic energy cutoff of planewaves
##ADDGRID = T includes a finer grid for the augmentation charge
##ENAUG = 606 augmentation charge cutoff
NELM = 70 # of ELM steps
EDIFF = 1E-05 stopping-criterion for ELM (1E-10 for NMR calculations)
LREAL = A Def: F real-space projection (deactivate for SP calculations)
##ROPT = -1E-5 #activate when LREAL=F
ALGO = Fast Davidson + RMM-DIIS algorithm
##NGX = 122; NGY = 118; NGZ = 72 #FFT mesh to avoid (wrap up) aliasing errors
##NGXF = NGYF = ; NGZF = #FFT mesh for charges (activate for CDD calculations)
Ionic relaxation
EDIFFG = -1E-02 stopping-criterion for IOM
NSW = 400 number of steps for IOM (deactivate for SP calculations)
IBRION = 2 ionic relax, Def(NSW=0 or -1): not moved: -1, MD: 0, quasi-New: 1,
CG: 2, freq: 5, dimer:44 (change for every type of calculations)
##NELMIN = 4 gives the minimum number of electronic SC steps, optimum value
is between 4 and 8 (activate when IBRION=1)
##NFREE = 10 number of ionic steps kept in the iteration history, optimum value is
between 10 and 20 (activate when IBRION=1). For frequency
calculations NFREE indicates the number of displacements used
for each direction and ion
##ISIF = 4 stress and relaxation, Def: 2 (only ions), 4 (ions and cell shape)
POTIM = 0.1000 time-step for ionic-motion (relaxations .1, frequency .015 or
transition state calculations .15 DIMER, .015 NEB)
Charge related values (activate for charged species):
##NELECT = 36 total number of electrons
##LMONO = T monopole corrections
##DIPOL = center of cell (in direct, fractional coordinates)
##EPSILON = dielectric constant of the medium
##EFIELD = applied electrostatic field
DOS related values:
ISMEAR = 1 broadening in eV -5: Blochl, -4: tet, -1: fermi, 0: gaus (1 k-point,
relaxations and NMR) (change for SP calculations)
SIGMA = 0.05 determines the width of the smearing in eV
##NEDOS = 903 number of grid points in DOS Def:301 (activate for SP calculations)
Write flags (activate all of them for SP calculations)
##LAECHG = T Def: F write core charge = AECCAR0 and
valence charge = AECCAR2
##LVTOT = T Def: F write LOCPOT, total local potential
##LELF = T Def: F write electronic localiz. function (ELFCAR)
##LORBIT = 12 writes DOCAR and PROCAR file with phase vectors
##LWAVE = T
LCHARG = F
```

Dipole corrections (do not activate for bulk phases, what about gas phase molecules?)

LDIPOL= T correct potential (dipole corrections)

IDIPOL = 3 1-x, 2-y, 3-z, 4-all directions

STM related values

##LPARD = T Evaluate partial (band and/or k-point) decomposed charge density.

##EINT = -2.5 Specifies the energy range of the bands that are used for the evaluation of the partial charge density.

##NBMOD = -3 Calculate the partial charge density for electrons with their eigenvalues in the range specified by EINT vs. Fermi energy.

6.5 Single Point Energy determination INCAR file

SYSTEM = Pt_SO2

Startparameter for this run:

```
PREC = Accurate Def: normal, accurate (activate for SP and NMR calculations), single
(STM calculations)
LASPH = T aspherical Exc in radial PAW
GGA = PE GGA type
##VOSKOWN = 1 Vosko Wilk Nusair interpolation (only for PW91)
ISPIN = 2 spin polarized calculation (1 for non spin polarized calculations)
##NUPDOWN = -1.0000 fix difference electrons up-down
## Pt
##MAGMOM = 1*0
##ICHARG= 1 how to construct the initial charge density, 1-file(activate if restarting from
non-spin polarised calculation) Def:2-atom 10-const

##LDAU = T
##LDAUTYPE = 2 Dudarev et al. approach
## O C H
##LDAUL = -1 -1 -1 no on-site: -1, p: 1, d: 2, f: 3
##LDAUU = 0.0 0.0 0.0U values
##LDAUJ = 0.0 0.0 0.0 J values
LMAXMIX = 4 for the calculation of band structures p:2, d: 4, f: 6
Parallelization
##LPLANE = T activate data distribution (only activate if NGZ is at least 3*(# of cores)/NPAR)
NCORE = 4 #NUMBER OF CORES PER ORBITAL
##NPAR = 4 NGZ=n*NPAR, NPAR=sqrt(cores) (do not use for NMR or FREQ calculations)
##KPAR = 5 # of compute nodes or k-points (try to make them the same by increasing compute
nodes), whichever is the smallest, divide by 2 or 4 if problems (N=#cores/KPAR)
(do not use for SP calculations)
##NBANDS = # of bands (increase if necessary) (# of cores = NBANDS/8)
Dispersion Interaction
IVDW = 12 Van der Waals corrections - DFT-D3 method
##VDW_S6 = 0.75 Global scaling factor PBE: 0.75
Electronic Relaxation
ENCUT = 400.0 kinetic energy cutoff of planewaves
##ADDGRID = T includes a finer grid for the augmentation charge
##ENAUG = 606 augmentation charge cutoff
NELM = 70 # of ELM steps
EDIFF = 1E-05 stopping-criterion for ELM (1E-10 for NMR calculations)
##LREAL = A Def: F real-space projection (deactivate for SP calculations)
##ROPT = -1E-5 -1E-5 #activate when LREAL=F
ALGO = Fast Davidson + RMM-DIIS algorithm
##NGX = 122; NGY = 118; NGZ = 72 #FFT mesh to avoid (wrap up) aliasing errors
##NGXF = ; NGYF = ; NGZF = #FFT mesh for charges (activate for CDD calculations)
Ionic relaxation
EDIFFG = -1E-02 stopping-criterion for IOM
##NSW = 400 number of steps for IOM (deactivate for SP calculations)
##IBRION = 2 ionic relax, Def(NSW=0 or -1): not moved: -1, MD: 0, quasi-New: 1, CG: 2, freq: 5,
dimer:44 (change for every type of calculations)
##NELMIN= 4 gives the minimum number of electronic SC steps, optimum value is between 4
and 8 (activate when IBRION=1)
##NFREE = 10 number of ionic steps kept in the iteration history, optimum value is between 10
and 20 (activate when IBRION=1). For frequency calculations NFREE indicates
the number of displacements used for each direction and ion
##ISIF = 4 stress and relaxation, Def: 2 (only ions), 4 (ions and cell shape)
POTIM = 0.1000 time-step for ionic-motion (relaxations .1, frequency .015 or transition state
calculations .15 DIMER, .015 NEB)
Charge related values (activate for charged species):
##NELECT = 36 total number of electrons
##LMONO = T monopole corrections
##DIPOL = center of cell (in direct, fractional coordinates)
##EPSILON = dielectric constant of the medium
##EFIELD = applied electrostatic field
DOS related values:
ISMEAR = -5 broadening in eV -5: Blochl, -4: tet, -1: fermi, 0: gaus (1 k-point, relaxations and
NMR) (change for SP calculations)
##SIGMA = 0.05 determines the width of the smearing in eV
NEDOS = 903 number of grid points in DOS Def:301 (activate for SP calculations)
Write flags (activate all of them for SP calculations)
LAECHG = T Def: F write core charge = AECCAR0 and valence charge = AECCAR2
LVTOT = T Def: F write LOCPOT, total local potential
LELF = T Def: F write electronic localiz. function (ELFCAR)
LORBIT = 12 writes DOCAR and PROCAR file with phase vectors
##LWAVE = T
LCHARG = T
Dipole corrections (do not activate for bulk phases, what about gas phase molecules?)
LDIPOL = T correct potential (dipole corrections)
```

IDIPOL	=	3	1-x, 2-y, 3-z, 4-all directions
STM related values			
##LPARD	=	T	Evaluate partial (band and/or k-point) decomposed charge density.
##EINT	=	-2.5	Specifies the energy range of the bands that are used for the evaluation of the partial charge density.
##NBMOD	=	-3	Calculate the partial charge density for electrons with there eigenvalues in the range specified by EINT vs. Fermi energy.

6.6 Bader Analysis files

The first step in Bader analysis involves the summation of the valence charge (AECCAR2) and the core-charge (AECCAR0) of a system. The Bader analysis is performed by using the chgsum.pl script as developed by Alberto Roldan [168] and presented below:

```
printf OUT " %18.11E" x @line1 . "\n", @line1;
# printf OUT " %18.11E", $_ for @line1;
# print OUT "\n";

}

close(IN1);
close(IN2);
close(OUT);
```

The Bader script file, as developed by the Henkelman group and written by Alberto Roldan is an interactive script and may be found [here](#) [144,146,147]

Examples of the three Bader analysis output files, for PtH₂O_(ad), i.e. ACF.dat, AVF.dat and BCF.dat, as discussed in Chapter 3 are:

ACF.dat						
#	X	Y	Z	CHARGE	MIN DIST	ATOMIC VOL
1	11.086903		6.401027	0.000000	10.011621	1.265654
2	9.701041		8.801410	0.000000	10.040576	1.265654
3	8.315179		6.401027	0.000000	10.082755	1.265654
4	6.929317		8.801410	0.000000	10.010281	1.265654
5	12.472765		4.000643	0.000000	10.063381	1.265654
6	11.086903		1.600259	0.000000	10.037921	1.265654
7	9.701041		4.000643	0.000000	10.055411	1.265654
8	2.771730		1.600259	0.000000	10.039366	1.265654
9	15.244489		8.801410	0.000000	10.071117	1.265654
10	13.858627		6.401027	0.000000	10.010281	1.265654
11	12.472765		8.801410	0.000000	10.043867	1.265654
12	5.543454		6.401027	0.000000	10.051488	1.265654
13	8.315178		1.600259	0.000000	10.047502	1.265654
14	6.929316		4.000643	0.000000	9.992640	1.265654
15	5.543454		1.600259	0.000000	10.064444	1.265654
16	4.157592		4.000643	0.000000	10.090205	1.265654
17	12.472760		7.201151	2.263102	9.907013	1.247264
18	11.086897		4.800768	2.263102	9.955936	1.247264
19	9.701035		7.201151	2.263102	9.960248	1.247264
20	2.771724		4.800768	2.263102	9.951578	1.247264
21	5.543449		0.000000	2.263102	9.947799	1.247264
22	4.157586		2.400384	2.263102	9.976119	1.247264
23	2.771724		0.000000	2.263102	9.963395	1.247264
24	1.385862		2.400384	2.263102	9.970870	1.247264
25	8.315173		4.800768	2.263102	9.925414	1.247264
26	6.929311		7.201151	2.263102	9.962234	1.247264
27	5.543449		4.800768	2.263102	9.933513	1.247264
28	4.157587		7.201151	2.263102	9.974184	1.247264
29	9.701035		2.400384	2.263102	9.960971	1.247264
30	8.315173		0.000000	2.263102	9.952705	1.247264
31	6.929311		2.400384	2.263102	9.915771	1.247264
32	0.000000		0.000000	2.263102	9.983398	1.247264
33	5.548665		3.199260	4.539458	9.950891	1.258668
34	4.153207		5.595659	4.522607	9.954269	1.252496
35	2.768980		3.192501	4.517904	9.972713	1.248934
36	12.469256		5.594123	4.521454	9.955243	1.251923

37	6.926489	0.792328	4.523690	9.961681	1.251500	15.124614
38	11.081764	7.996696	4.522261	9.956428	1.252436	15.107257
39	4.153080	0.796284	4.518504	9.962090	1.249726	15.116330
40	13.856316	7.995083	4.521247	9.960383	1.252447	15.119880
41	9.698241	5.595813	4.522653	9.955663	1.251584	15.095028
42	8.308432	3.195929	4.532082	9.953624	1.245943	15.107257
43	6.926755	5.589505	4.534087	9.967221	1.261350	15.160905
44	11.083577	3.190965	4.516452	9.955831	1.247037	15.079249
45	8.308172	7.995822	4.517097	9.959493	1.246965	15.101734
46	1.382858	0.794124	4.526065	9.958470	1.249193	15.091478
47	5.542002	7.997320	4.517858	9.956565	1.250554	15.085166
48	9.700414	0.795218	4.517881	9.960939	1.250704	15.103706
49	6.907215	3.980604	6.851961	9.918366	1.216749	17.743541
50	5.526297	1.568372	6.821763	10.038538	1.270772	38.991215
51	4.130191	3.988535	6.820172	10.061765	1.270547	38.911531
52	8.313388	1.572559	6.821140	10.083706	1.272879	36.559664
53	5.527046	6.400931	6.817590	10.060611	1.276758	37.865380
54	15.237732	8.789360	6.823999	10.034241	1.278380	50.314261
55	13.846964	6.390234	6.825313	10.031854	1.282567	52.087432
56	12.466135	8.783398	6.826189	10.057912	1.277988	50.285070
57	2.761336	1.585694	6.825912	10.052829	1.281888	51.938715
58	12.464150	3.986874	6.823192	10.041711	1.262971	50.119785
59	11.079114	1.587057	6.826788	10.058436	1.279332	49.631818
60	9.709406	3.989918	6.816968	10.094759	1.276807	34.035016
61	9.692116	8.786221	6.823999	10.058438	1.276222	49.741087
62	8.317296	6.400854	6.823653	10.092455	1.270084	35.203060
63	6.922482	8.789130	6.826281	10.057043	1.278423	49.748582
64	11.080162	6.388372	6.826281	10.054376	1.278313	49.148584
65	7.857539	3.400096	9.297384	0.333762	0.101805	114.438347
66	7.546153	4.922669	9.273779	0.355500	0.071967	113.099100
67	7.118376	4.040768	9.228665	7.218199	0.717747	148.830364

VACUUM CHARGE: 0.0000
VACUUM VOLUME: 0.0000
NUMBER OF ELECTRONS: 648.0000

AVF.dat

Atom	Volume(s)	Atom	Volume(s)	Atom	Volume(s)	Atom	Volume(s)

1	55	19	47	37	48	55	16
2	43	20	12	38	51	56	53
3	41	21	44	39	33	57	24
4	23	22	28	40	22	58	10
5	11	23	27	41	50	59	4
6	6	24	8	42	49	60	58
7	52	25	46	43	35	61	38
8	25	26	30	44	66	62	37
9	1	27	29	45	36	63	7
10	17	28	18	46	3	64	59
11	54	29	62	47	21	65	60
12	19	30	61	48	65	66	31
13	57	31	45	49	32	67	26
14	42	32	2	50	39		
15	40	33	34	51	15		
16	13	34	14	52	56		
17	64	35	9	53	20		
18	63	36	67	54	5		

BCF.dat

#	X	Y	Z	CHARGE	ATOM	DISTANCE
1	15.2445		8.8014	0.0000	10.0711	9 0.0000
2	0.0000		0.0000	2.2284	9.9834	32 0.0347
3	1.3859		0.8001	4.5336	9.9585	46 0.0101
4	11.0869		1.6003	6.8389	10.0584	59 0.0195
5	15.2445		8.8014	6.8389	10.0342	54 0.0203
6	11.0869		1.6003	0.0000	10.0379	6 0.0000
7	6.9293		8.8014	6.8389	10.0570	63 0.0189
8	1.3859		2.4004	2.2284	9.9709	24 0.0347
9	2.7717		3.2005	4.5336	9.9727	35 0.0179
10	12.4728		4.0006	6.8389	10.0417	58 0.0226
11	12.4728		4.0006	0.0000	10.0634	5 0.0000
12	2.7717		4.8008	2.2284	9.9516	20 0.0347
13	4.1576		4.0006	0.0000	10.0902	16 0.0000
14	4.1576		5.6009	4.5336	9.9543	34 0.0130
15	4.1576		4.0006	6.8389	10.0618	51 0.0353
16	13.8586		6.4010	6.8389	10.0319	55 0.0209
17	13.8586		6.4010	0.0000	10.0103	10 0.0000
18	4.1576		7.2012	2.2284	9.9742	28 0.0347
19	5.5434		6.4010	0.0000	10.0515	12 0.0000
20	5.5434		6.4010	6.8389	10.0606	53 0.0269
21	5.5434		8.0013	4.5336	9.9566	47 0.0163
22	13.8586		8.0013	4.5336	9.9604	40 0.0140
23	6.9293		8.8014	0.0000	10.0103	4 0.0000
24	2.7717		1.6003	6.8389	10.0528	57 0.0221
25	2.7717		1.6003	0.0000	10.0394	8 0.0000
26	7.1218		4.0673	9.2210	7.2182	67 0.0279
27	2.7717		0.0000	2.2284	9.9634	23 0.0347
28	4.1576		2.4004	2.2284	9.9761	22 0.0347
29	5.5434		4.8008	2.2284	9.9335	27 0.0347
30	6.9293		7.2012	2.2284	9.9622	26 0.0347
31	7.5452		4.9341	9.2978	0.3555	66 0.0266
32	6.9293		4.0006	6.8389	9.9184	49 0.0326
33	4.1576		0.8001	4.5336	9.9621	39 0.0163
34	5.5434		3.2005	4.5336	9.9509	33 0.0079
35	6.9293		5.6009	4.5336	9.9672	43 0.0117
36	8.3152		8.0013	4.5336	9.9595	45 0.0188
37	8.3152		6.4010	6.8389	10.0925	62 0.0154
38	9.7010		8.8014	6.8389	10.0584	61 0.0231
39	5.5434		1.6003	6.8389	10.0385	50 0.0400
40	5.5434		1.6003	0.0000	10.0644	15 0.0000
41	8.3152		6.4010	0.0000	10.0828	3 0.0000
42	6.9293		4.0006	0.0000	9.9926	14 0.0000
43	9.7010		8.8014	0.0000	10.0406	2 0.0000
44	5.5434		0.0000	2.2284	9.9478	21 0.0347
45	6.9293		2.4004	2.2284	9.9158	31 0.0347
46	8.3152		4.8008	2.2284	9.9254	25 0.0347
47	9.7010		7.2012	2.2284	9.9602	19 0.0347
48	6.9293		0.8001	4.5336	9.9617	37 0.0130
49	8.3152		3.2005	4.5336	9.9536	42 0.0083
50	9.7010		5.6009	4.5336	9.9557	41 0.0124
51	11.0869		8.0013	4.5336	9.9564	38 0.0133
52	9.7010		4.0006	0.0000	10.0554	7 0.0000
53	12.4728		8.8014	6.8389	10.0579	56 0.0230
54	12.4728		8.8014	0.0000	10.0439	11 0.0000
55	11.0869		6.4010	0.0000	10.0116	1 0.0000
56	8.3152		1.6003	6.8389	10.0837	52 0.0329
57	8.3152		1.6003	0.0000	10.0475	13 0.0000
58	9.7010		4.0006	6.8389	10.0948	60 0.0258
59	11.0869		6.4010	6.8389	10.0544	64 0.0191
60	7.8147		3.4005	9.2978	0.3338	65 0.0428
61	8.3152		0.0000	2.2284	9.9527	30 0.0347
62	9.7010		2.4004	2.2284	9.9610	29 0.0347
63	11.0869		4.8008	2.2284	9.9559	18 0.0347
64	12.4728		7.2012	2.2284	9.9070	17 0.0347
65	9.7010		0.8001	4.5336	9.9609	48 0.0165
66	11.0869		3.2005	4.5336	9.9558	44 0.0199
67	12.4728		5.6009	4.5336	9.9552	36 0.0144