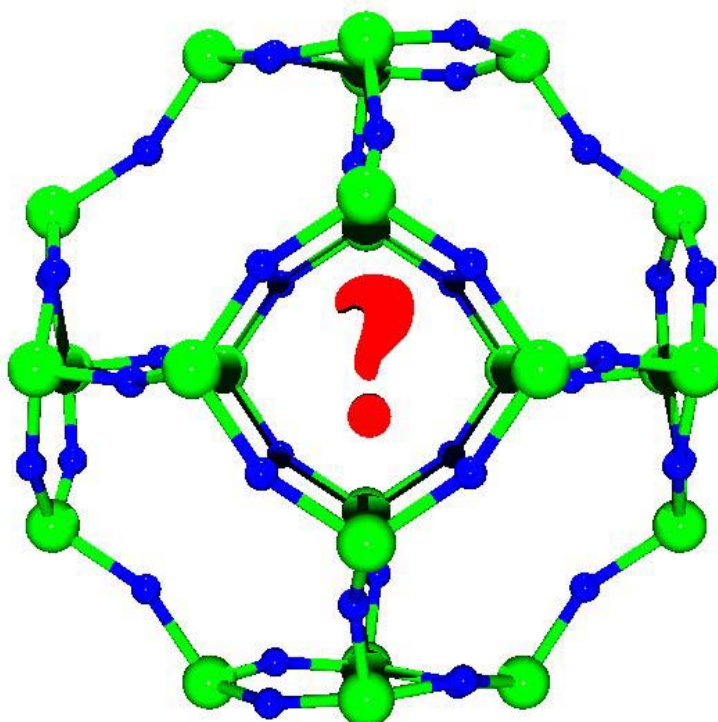


Chapter 5

MODELLING SULPHUR CLUSTERS IN ULTRAMARINE

in

**Aspects of solid-state chemistry of fly ash and ultramarine
pigments**



5. MODELLING SULPHUR CLUSTERS IN ULTRAMARINE

5.1. Introduction

Ultramarine pigments come in green, blue, greenish blue, reddish blue, violet, pink and red variants.¹⁻⁷ Several chromophores are present in the aluminosilicate zeolite-type framework of the ultramarine species. S_2^- is the yellow chromophore^{2,5,8-10} in ultramarine and S_3^- (Figure 5-1) is the blue chromophore.^{2,5,8,9} Ultramarine green is an ultramarine species in which the yellow and blue chromophores are present in such a ratio as to allow the green colour to be observed.

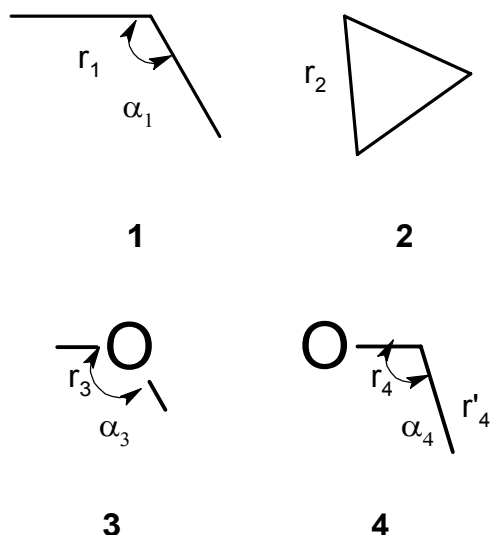


Figure 5-1: S_3 , S_2O and SOS species: (1) Open S_3 (C_{2v}), (2) Closed S_3 (D_{3h}), (3) SOS (C_{2v}), (4) S_2O (C_s)

As mentioned in Chapter 3 ultramarine blue is synthesised in two steps, a reduction step followed by an oxidation step.^{1,2,5,8,9,11-14} The nature of these steps is, however, disputed. Some authors suggested Equation 4-1,^{2,5,8,9} whereas others supported the existence of doubly charged species according to Equations 4-2 and 4-3.^{1,11-13} The oxidation of ultramarine green to ultramarine blue is related to an increasing S_3^-/S_2^- ratio (Chapter 3),^{2,5,8,9,14} in support of Equation 4-1. Beardsley and Whiting¹² described the formation of ultramarine blue with oxygen as oxidising agent and introduced the use of SO_2 in the production thereof.¹² Gorshtein^{11,13} (Equations 4-2 and 4-3) successfully explained the formation of Na_2SO_4 and the role

of SO_2 , noted by Tarling and others¹⁵ and Gobelz and others.⁸ This explanation was based on the identification of S_3^{2-} and S_2^{2-} as the yellow, and $\text{S}_3^{\cdot-}$ and $\text{S}_2^{\cdot-}$ as the blue chromophores. Other evidence identified $\text{S}_3^{\cdot-}$ as responsible for the blue colour and $\text{S}_2^{\cdot-}$ for yellow.^{2,5,8,9,16} No spectroscopic evidence of the doubly charged species was available in the literature (Chapter 4).¹⁴ Köhler and others¹⁰ synthesized ultramarine yellow from the thiocyanide derivative of sodalite. They¹⁰ confirmed that the yellow chromophore was $\text{S}_2^{\cdot-}$ and that oxidation led to the formation of ultramarine green, with the simultaneous formation of $\text{S}_3^{\cdot-}$.¹⁰ The evidence supported the formation of $\text{S}_3^{\cdot-}$ from $\text{S}_2^{\cdot-}$ rather than from S_3^{2-} . On the other hand, Weller and others,¹⁷ presented evidence that of a doubly charged species was involved, as described on pages 58 and 59. The high ratio of sulphur atoms to unpaired electrons found by Hofmann and others⁶ in the ultramarine green pigment supported the possible existence of doubly charged non-radical sulphide species. This conclusion was not generally accepted.¹⁸

The ultramarine red chromophore had been identified as an isomer of the S_4 molecule (Figure 5-2).^{1,2,5,19} The S_4 molecule could possibly form from $\text{S}_3^{\cdot-}$ and $\text{S}^{+\cdot}$ in a concerted reaction.²⁰ The feasibility of single-step concerted reactions could be evaluated by examining the phase symmetry of the molecular orbitals, by the methods of Fukui^{21,22} and of Woodward and Hoffmann.²³⁻²⁶ The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were assumed to feature in reactions to form new bonds. For a reaction to take place the HOMO (LUMO) of the attacked species and the LUMO (HOMO) of the attacking species must have had the same phase symmetry. This condition allowed regions of the same phase in the molecular orbitals to overlap and to form new bonding and anti-bonding molecular orbitals provided favourable overlap occurred. Sannigrahi and Grein²⁷ used the Woodward-Hoffmann methodology to show that the formation of S_4^{2+} from S_2^+ was not allowed.

The molecular orbitals of $\text{S}^{+\cdot}$, $\text{S}_2^{\cdot-}$, and $\text{S}_3^{\cdot-}$ were computed in this work in order to use a Woodward-Hoffmann analysis to evaluate the feasibility of the formation of some of the S_4 isomers. S_2 , S_2^{2-} , S_3 , and S_3^{2-} were also modelled in an effort to find the most stable sulphur species. These results might confirm that green ultramarine yielded blue ultramarine by the formation of $\text{S}_2^{\cdot-}$, $\text{S}_3^{\cdot-}$ from S_2^{2-} , S_3^{2-} .¹¹⁻¹³

5.2. Experimental data

Naudé^{28,29} studied the rotational substructure of the vibrational spectrum of S_2 and determined the bond length to be 1.893 Å. Based on the absorption band fine structure between 160 and 190 nm Maeder and Miescher³⁰ calculated a vibrational frequency of 724 cm^{-1} , for S_2 . $S_2^{\cdot-}$ had a Raman band at 590 cm^{-1} ,^{2,5} and S_2^{2-} a band at 451 cm^{-1} .³¹

Hopkins and others³² observed the S_3 molecule as part of an electric discharge reaction and observed Raman bands at 585, 490, and 650 cm^{-1} . Brabson and others³³ recorded the infrared spectrum of S_3 in a solid argon matrix (Table 5-1). They concluded that the structure of S_3 was the C_{2v} open geometry, with an angle of $116 \pm 2^\circ$.³³ Lenain and others³⁴ studied the Raman spectra of S_3 and also concluded that the C_{2v} isomer was the observed species (Table 5-1). Clark and Cobbold² observed both the Raman and infrared bands for $S_3^{\cdot-}$ (Table 5-1). Janz and others^{31,35,36} studied several polysulphides. For BaS_3 the S_3^{2-} structure was said to be C_{2v} with vibrational modes at 227/238 (R), 458 (R,IR), and 476 cm^{-1} (R,IR).³⁵ For K_2S_3 the same interpretation held, with the stretching modes accidentally degenerate: 238 (R) and 466 cm^{-1} (R,IR).³⁶

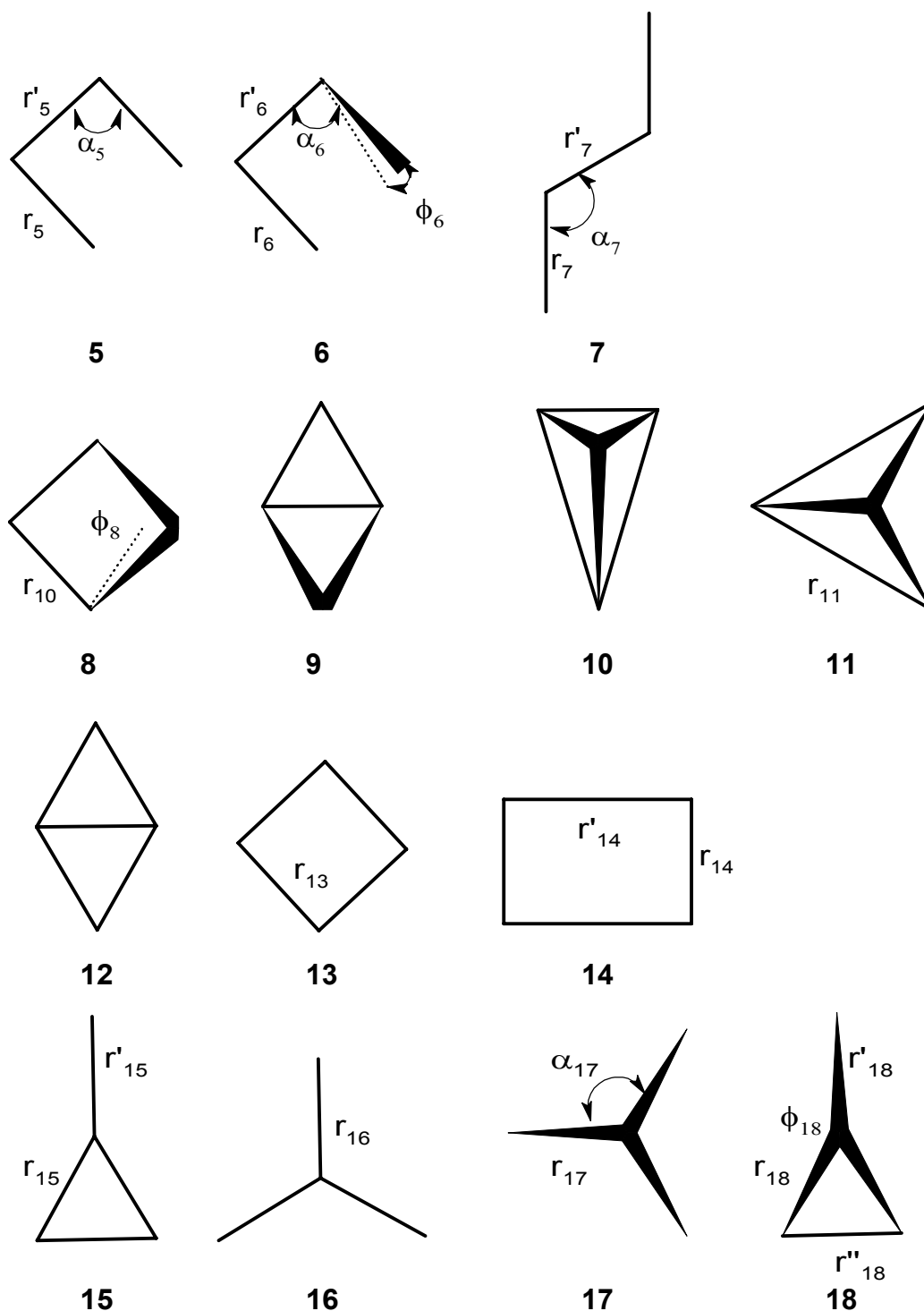


Figure 5-2: Isomers of S_4 : (5) Cis Chain (C_{2v}), (6) Gauche Chain (C_2), (7) Trans Chain (C_{2h}), (8) Puckered Ring (D_{2d}), (9) Butterfly (D_{2d}), (10) Tetrahedral (Geometry optimised) (D_{2d}), (11) Tetrahedral (T_d), (12) Double Triangle (D_{4h}), (13) Square Planar (D_{4h}), (14) Rectangle (D_{2h}), (15) Exocyclic (C_{2v}), (16) Branched Chain (D_{3h}), (17) Pyramidal (C_s), (18) Bent exocyclic (C_s)

Table 5-1: Experimental characteristics of S_3 , S_3^- , and S_3^{2-}

	Reference	Assignment	Infrared cm^{-1}	Raman cm^{-1}
S_3	[32]	ν_1		585
		$\nu_2 ?$	495 or 310	490
		ν_3		650
	[33]	ν_1		583
	[33,35]	ν_2	680	
	[33,37]	Vibrational progression	340 450	
	[34]	ν_1		575
		ν_2 ν_3		256 656
S_3^-	[2,5]	ν_1		548
	[2]	ν_3	582	
	[2]	ν_1	547	
	[38]	ν_2		232
S_3^{2-}	[35]	ν_1 or ν_3	457	458
		ν_2		227/238
		ν_1 or ν_3	476	476
	[36]	ν_1 and ν_3		466
		ν_2		238

5.3. Molecular Modelling

When doing molecular modelling the objectives need to be clear. In the work on sulphur compounds the shape of the molecular orbitals was important because it dictated the reactivity of the species under consideration and was used in the Woodward-Hofmann analyses. The energies were also important as an estimate of the relative stability of the ionic states of S_2 and S_3 . A potential energy surface specified the classical potential energy as a function of molecular structure.³⁹ This concept was useful for the comparison of the possible geometrical isomers. The potential energy surface was inspected for S_2 , S_2^- , S_2^{2-} , S_3 , S_3^- , and S_3^{2-} in an effort to find the most favourable oxidation states of these species, and to obtain the molecular orbitals for use in a Woodward Hoffmann analysis.

5.4. Results

The geometry optimisation gave reasonable results, compared to literature values (Table 5-2). As the charge on the S_2 species became more negative the bond distance increased (Table 5-2). The geometry of the closed $S_3^{\cdot-}$ isomer did not optimise to the desired D_{3h} symmetry and the bond length was therefore set to the average of the values found in the literature (Table 5-2). The geometry of the closed S_3^{2-} isomer optimised to unrealistically long bond lengths, and the bond distance was set to 2.24 Å.⁴⁰ The nature of this optimisation anomaly was not investigated.

The singly charged anions of both S_2 and S_3 were found to be the most stable states relative to the neutral and doubly charged states (Tables 5-3 and 5-4). The reaction that transformed ultramarine green to blue was exothermic.¹² The calculated results supported the proposal that this reaction involved the transition from S_2^{2-} , S_3^{2-} to $S_2^{\cdot-}$, $S_3^{\cdot-}$.^{1,11-13} The computational results at the SCF UHF with the 6-311G** basis set and MP2 extension at the minimum energy indicated that the open, C_{2v} , structure was the most stable isomer for the $S_3^{\cdot-}$ molecule (Table 5-4). In fact, at this level, the closed, D_{3h} , $S_3^{\cdot-}$ geometry was shown to be a transition state. Since the $S_3^{\cdot-}$ molecule was the blue chromophore in ultramarine blue,^{1,2,5,8,9} the geometry of this important stable radical polysulphide was calculated. This geometry could now be used in modelling the ultramarine pigment itself,⁴¹ and could assist in crystallographic interpretation.¹⁵ The calculated vibrational frequencies for S_2 , $S_2^{\cdot-}$, and S_2^{2-} were in good agreement with the experimental values (Table 5-5). For S_2^{2-} the unscaled frequencies fit best (Table 5-5). The vibrational frequency decreased with an increase in the negative charge on the S_2 molecule as expected from the reverse trend in the bond distances (Table 5-2). After applying the scale factor of 0.87 to calculated frequencies (Table 5-6) of the open S_3 isomer, they corresponded well with experimental values (Tables 5-1 and 5-6). The scaled vibrational frequencies of the closed, D_{3h} , S_3 isomer (Table 5-7) agreed with the experimental values as well. The calculated vibrational frequencies of $S_3^{\cdot-}$ were less accurate (Table 5-8). The antisymmetric stretching frequency was underestimated. Again no scaling was needed as discussed in the conclusion. For S_3^{2-} , the vibrational frequencies were close to the experimental values without scaling (Table 5-8).

Table 5-2: Bond lengths (Å) and angles (°) for S₂ and S₃ species

Structure name	Symmetry	Structural parameter ^a	This work	Average from literature ^b	References
S ₂	D _{∞h}	<i>r</i>	1.88	1.91(2)	[42-44]
S ₂ ^{••}	D _{∞h}	<i>r</i>	2.01	2.12(8)	[42,45]
S ₂ ²⁻	D _{∞h}	<i>r</i>	2.21 (2.80)		
Singlet open S ₃	C _{2v}	<i>r</i> ₁	1.90	1.98(2)	[40,43,44,46-51]
		<i>α</i> ₁	117	116.6(7)	"
Singlet closed S ₃	D _{3h}	<i>r</i> ₂	2.08	2.12(2)	"
³ A ₂ open S ₃	C _{2v}	<i>r</i> ₁	1.99	2.00(4)	[43,47]
		<i>α</i> ₁	93	93(2)	"
Open S ₃ ^{••}	C _{2v}	<i>r</i> ₁	2.00	2.02(3)	[40,45,51]
		<i>α</i> ₁	115	113(2)	"
Closed S ₃ ^{••}	D _{3h}	<i>r</i> ₂	2.24	2.241(5)	[40,51]
Open S ₃ ²⁻	C _{2v}	<i>r</i> ₁	2.13	2.08(8)	[40,45]
		<i>α</i> ₁	113	109(6)	"
Closed S ₃ ²⁻	D _{3h}	<i>r</i> ₂	2.24	2.244	[40]

a. As defined in Figure 5-1

b. The value given is the average from several literature values, the number in brackets denotes one standard deviation of the mean

Table 5-3: Relative energy (kJ/mol) results for S₂^a

Structure name	This work
S ₂ singlet	146
S ₂ triplet	113
S ₂ ^{••}	0
S ₂ ²⁻ singlet	427
S ₂ ²⁻ triplet	632 i ^b

a. The energy of the most stable isomer was set equal to zero and the other energies are reported relative to this most stable state

b. i indicates that the species has an imaginary frequency

Table 5-4: Relative energy (kJ/mol) results for S₃^a

Structure number	Structure name	This work
1	Open S ₃ Singlet	197
2	Closed S ₃ Singlet	234
1	Open S ₃ Triplet	297
2	Closed S ₃ Triplet	473 i ^b
1	Open S ₃ ⁻	0
2	Closed S ₃ ⁻	192 i
2	Closed S ₃ ²⁻ Singlet	720 i
1	Open S ₃ ²⁻ Singlet	331
2	Closed S ₃ ²⁻ Triplet	682 i
1	Open S ₃ ²⁻ Triplet	577 i

- a. The energy of the most stable isomer was set equal to zero and the other energies are reported relative to this most stable state
 b. i indicates that the species has an imaginary frequency

Table 5-5: Vibrational frequencies in cm⁻¹ of S₂ stretching vibration

	This work	Scaled values	Experimental	References	Ratio of experimental and this work
Singlet (triplet) S ₂	791 (790) ^a	687	724	[30]	0.92
Doublet S ₂ ⁻	615	535	590	[2][5]	0.96
Singlet S ₂ ²⁻	426	371	451	[31]	1.06

- a. Value in brackets is for the triplet state

Table 5-6: Vibrational frequencies in cm⁻¹ of open S₃ (1)

Mode	Description	Symmetry	This work	Scaled values ^a	Experimental values ³⁴	Spectroscopic activity ^b	Ratio of experimental and this work
v ₁	Symmetric stretch	a ₁	654 (627) 294	569	575	R, IR	0.88 (0.92)
v ₂	Bending	a ₁	(211) ^c	256	256	R, IR	0.87 (1.21)
v ₃	Antisymmetric stretch	b ₂	737 (490)	641	656	R, IR	0.89 (1.34)

- a. Scaled with a scale factor of 0.87³³
 b. R: Raman active, IR: Infrared active
 c. Values in brackets are for the triplet state

Table 5-7: Vibrational frequencies in cm^{-1} of closed S_3 (2)

Mode	Description	Symmetry	This work	Scaled values ^a	Experimental values	Spectroscopic activity ^b	Ratio of experimental and this work
ν_1	Symmetric Deformation	a_1'	662	576	583, ³³ 585, ³² 575 ³⁴	R	0.88, 0.88, 0.87
ν_2	Stretch	e'	500	435	450, ^{33,37} 490 ³²	R, IR	0.90, 0.98

a. Scaled with a scale factor of 0.87³³

b. R: Raman active, IR: Infrared active

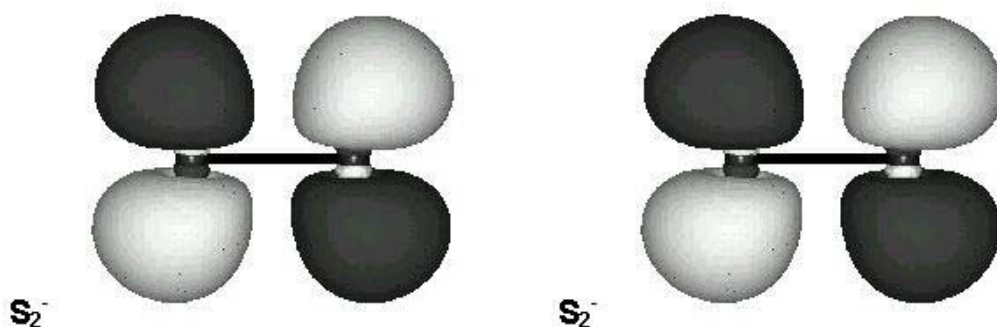
Table 5-8: Vibrational frequencies in cm^{-1} of negatively charged open S_3 (1)

Mode	Description	Symmetry	Doublet S_3^{2-}	Experimental values for S_3^{2-}	Singlet open S_3^{2-}	Experimental ³⁵ values for S_3^{2-}	Spectroscopic activity ^a
ν_1	Symmetric Stretch	a_1	558	548 ² (0.98)	459	458 (1.00)	R, IR
ν_2	Bending	a_1	250	232 ³⁸ (0.93)	202	227 (1.12) / 238 (1.18)	R, IR
ν_3	Antisymmetric Stretch	b_2	449	582 ² (1.30)	496	476	R, IR

a. R: Raman active, IR: Infrared active

b. Values in brackets represent the ratio between the experimental frequency and the calculated frequency

Molecular modelling of the polysulphide species was done in order to obtain a molecular orbital picture of S_2^{2-} (Figure 5-3), and S^{2+} and S_3^{2-} (Figure 5-4). HyperChem⁵² was used to model the S_2^{2-} and S_3^{2-} structures by the ZINDO/1 semi-empirical method, and self-consistent-field unrestricted Hartree-Fock simulation using a 6-311G** *ab initio* basis set extended by MP2 correlation energy. The ZINDO/1 results confirmed the character of the highest occupied molecular orbital for both open (b_1) and closed (a_2') S_3^{2-} of a previous pictorial model²⁰ and the work of Koch and others⁴⁰ (Figure 5-4).

**Figure 5-3: Highest occupied (left) and lowest unoccupied (right) molecular orbital of S_2^{2-}**

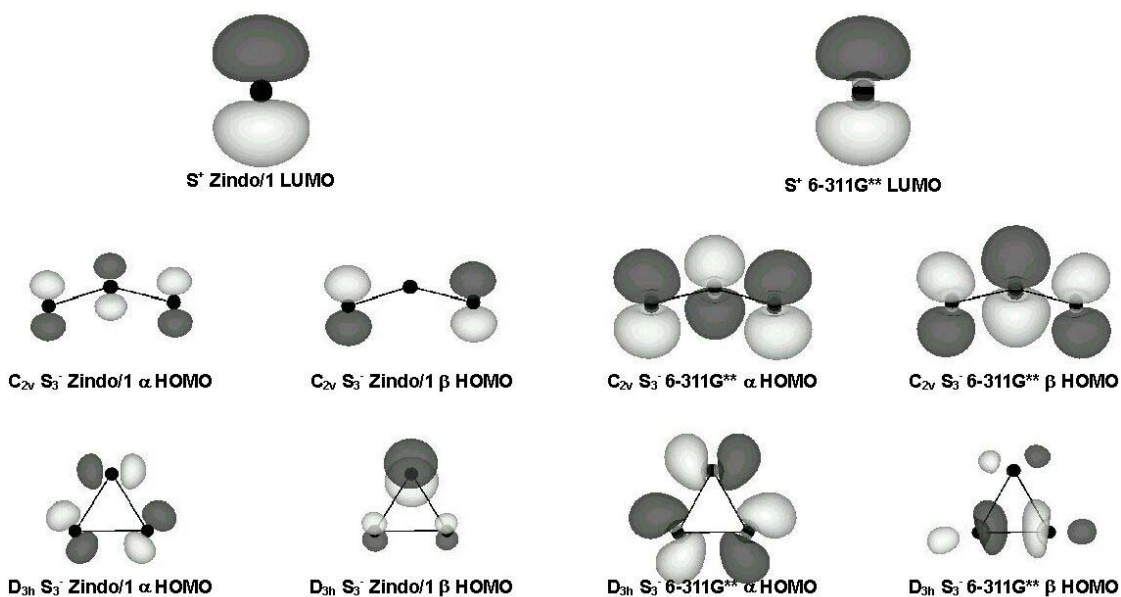


Figure 5-4: Molecular orbital diagram of S^{+} (ZINDO/1 and 6-311G LUMO) and S_3^{-} (ZINDO/1 and 6-311G** α and β HOMO)**

It was assumed that S^{+} (Figure 5-4) attacked the S_3 (Figure 5-4) species in a concerted reaction to form S_4 (Figure 5-2). This was tested by means of the frontier orbital symmetry theory of Woodward and Hoffmann.²³⁻²⁵ The HOMO of S_3^{-} (Figure 5-4) was placed near the LUMO of S^{+} (Figure 5-4) in such a way as to ensure that lobes of the same phase overlapped to form σ -orbitals. The charge distribution on the sulphur atoms of the $C_{2v} S_3^{-}$ isomer indicated that the central sulphur atom was positively charged (Figure 5-5), therefore attack of S^{+} was unlikely to occur on this atom. To test whether the electrostatic charges would be detrimental to this form of attack the distance between the fourth sulphur atom and the central sulphur atom, in the branched chain isomer, was increased (Figure 5-5), with the result that the original electrostatic charge distribution was induced in the $C_{2v} S_3^{-}$ moiety. Electrostatics did therefore not preclude the attack of S^{+} on the central sulphur of the open, C_{2v}, S_3^{-} isomer.

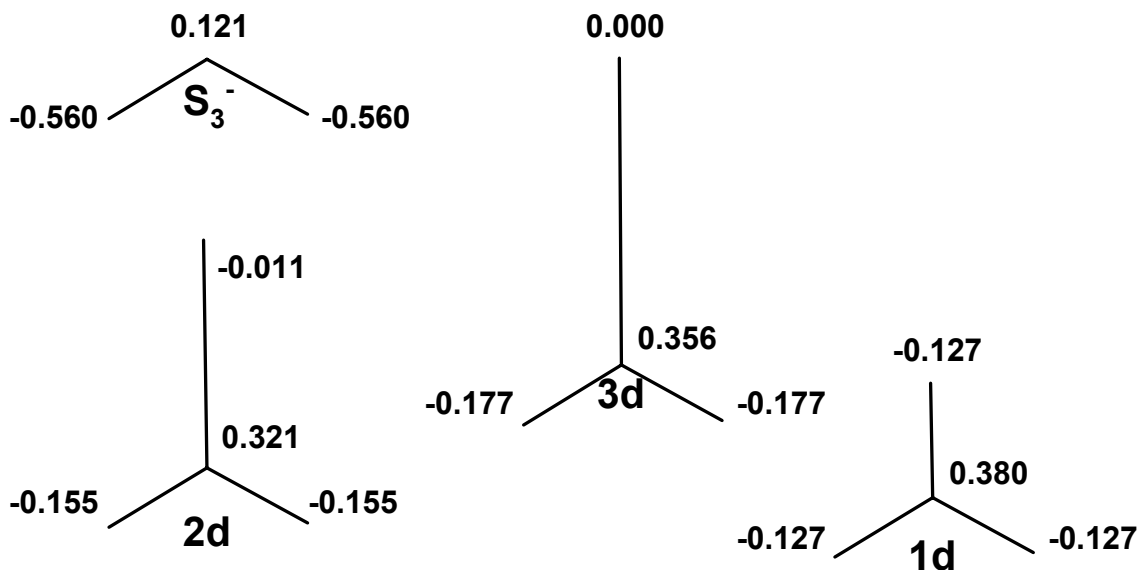


Figure 5-5: Charge distribution in S_3^- and branched chain S_4 at thrice (3d), twice (2d) and at its normal distance (1d), showing that the positive charge on the central sulphur atom in S_3^- is not necessarily a problem in the formation of branched chain S_4 from S_3^- and S^+

A Woodward-Hoffmann analysis at the ZINDO/1 level showed that the puckered S_4 ring, pyramidal branched chain S_4 , gauche S_4 chain and bent exocyclic S_4 isomers were possible products of the concerted reaction of S^+ and S_3^- . At the 6-311G** level of theory, the highest occupied molecular orbital of the closed, D_{3h} , S_3^- isomer precluded the formation of the bent exocyclic S_4 isomer. The symmetry of the S_2^- highest occupied and lowest unoccupied molecular orbital (Figure 5-3), furthermore, predicted that the closed, D_{3h} , S_3^- isomer could not be formed in a concerted way from S_2^- .

5.5. Discussion

Ab initio results should not be accepted at face value because of the approximations made during the analysis. Strictly speaking, *ab initio* computations are only relevant to gas phase molecules in vacuum at 0 K. The environment created by the sodium counterions and the aluminosilicate framework was not taken into account. The structure of the aluminosilicate framework did ensure that the sulphur chromophores

acted independently as molecules and did not form part of an extended sulphur-based "molecule".

The calculated vibrational frequency of S_2 at 793 cm^{-1} , scaled (0.87) to 690 cm^{-1} , was in reasonable agreement with the experimental value of 724 cm^{-1} (Table 5-5). The bond length of 1.88 \AA was in close agreement with the experimental 1.893 \AA .^{28,29} Heinemann and others⁴² calculated the vibrational frequency of S_2^* to be 582 cm^{-1} , close to the experimental value (Table 5-5). The current value was not far from the expected value (Table 5-5). Heinemann and others⁴² calculated that the triplet S_2 molecule was less energetic than the S_2^* molecule. The current results confirmed this.

Rau and others⁵³ suggested that sulphur allotrope tautomers with an energy difference less than 33 kJ/mol contributed appreciably to the vapour composition of that particular species at temperatures between 823 and $1\ 273\text{ K}$, the so-called tautomeric occurrence[†]. This was suggested on the basis of the work of Pauling,⁵⁴ who mentioned the estimate of tautomeric occurrence at 41 kJ/mol . Taking into account the reliability of the computed values, sulphur allotropic isomers with an energy difference of less than 41 kJ/mol relative to the most stable isomer, in this work, should be present in appreciable amounts.

The bond angle calculated for the open S_3 isomer was 117° , within the experimental range.³³ The question of whether the open, C_{2v} ,^{40,43,47,48,50,51} or closed, D_{3h} ,^{42,50,51,55,56} S_3 isomer was the more stable seemed to be an open question, since several methods gave contradictory results, depending on the methodology applied to the problem. The open, C_{2v} , S_3 isomer was calculated to be the most stable in this work. The computed closed, D_{3h} , S_3 isomer had an energy only 38 kJ/mol higher than the open isomer, therefore both these isomers should be observable (Table 5-4) and probably were (Table 5-6 and Table 5-7).

[†] The term tautomer is used to describe a geometric isomer in the cited reference. The term tautomeric occurrence therefore implies the possible presence of different geometric isomers.

From literature it seemed as though the open, C_{2v} ,^{40,49} S_3^- isomer was deemed to be more stable than the closed, D_{3h} , isomer. This was confirmed in the current work. The scale factor of 0.87, suggested by Brabson and others,³³ worked well for the neutral sulphur molecules (Tables 5-5, 5-6 and 5-7), but failed for the ionised species (Tables 5-5 and 5-8). A scaling factor closer to or larger than 1.00 seemed more appropriate.

The assumption that the S_4 molecules were formed by concerted reactions of S_3^- and S^{+} was theoretically useful, although the existence of the S^{+} was unlikely. Berkowitz and Chupka⁵⁷ studied the dissociation of S_2 and determined the dissociation energy to be 423 ± 1 kJ/mol from the photoionization threshold of 14.74 ± 0.01 eV for Equation 5-1. The existence of S^{+} , therefore, seemed plausible.



Based on the fact that the tetrahedral geometry had an open-shell electronic configuration, Salahub and others⁴⁹ ruled out the tetrahedral geometry as the ground state of S_4 by $X\alpha$ -scattered wave calculations. Landman and De Waal also reached this conclusion based on Woodward-Hoffmann selection rules,²⁰ and it was verified in the current work.

5.6. Conclusion

At the SCF UHF level of theory with 6-311G** as basis set and a MP2 energy correction the open, C_{2v} , structure was found to be the most stable isomer for the S_3^- molecule, which was the blue chromophore in ultramarine. The closed, D_{3h} , geometry was calculated to be a transition state (Table 5-4). For both S_2 and S_3 the singly charged anions were calculated to be the most stable state, in relation to the neutral and doubly charged states (Table 5-3, Table 5-4). In light of the evidence that the reaction transforming the ultramarine green to the desirable ultramarine blue was exothermic,¹² the current results supported the proposal that this reaction involved the transition from S_2^{2-} , S_3^{2-} to S_2^{-} , S_3^{-} .^{1,11-13}

Woodward-Hoffmann orbital analyses based on ZINDO/1 suggested that the product of a concerted reaction between S_3^- and S^+ was either the puckered S_4 ring, pyramidal S_4 , gauche chain S_4 or bent exocyclic S_4 structure. At the 6-311G** level the formation of the bent exocyclic S_4 isomer was excluded.

The symmetry of the S_2^- orbitals (Figure 5-3), did not favour the formation of $D_{3h} S_3^-$ species from S_2^- in a concerted way.

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