

## Article

# Raman-Validated Macromolecular Model of SG Coking Coal: ESP–FMO Mapping Unravels Site-Selective Oxidation in Combustion

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## Abstract

Based on comprehensive experimental datasets—proximate/ultimate analyses, XPS, solid-state <sup>13</sup>C NMR, and Raman spectroscopy—we constructed and optimized a compositionally faithful macromolecular model of SG coking coal. Using density-functional theory (DFT) calculations, we simulated electrostatic-potential (ESP) fields and frontier molecular orbitals (FMO) to probe elementary oxidation steps relevant to combustion, and focused on how heteroatom speciation and carbon ordering govern site-selective reactivity. Employing multi-peak deconvolution and parameter synthesis, we obtained an aromatic fraction  $f_a = 76.56\%$ , a bridgehead-to-periphery ratio  $X_{BP} = 0.215$ , and Raman indices  $I_{D1}/I_G \approx 1.45$  (area) with FWHM(G)  $\approx 86.7 \text{ cm}^{-1}$ ; the model composition  $C_{190}H_{144}N_2O_{21}S$  and its predicted <sup>13</sup>C NMR envelope validated the structural assignment against experiment. ESP–FMO synergy revealed electron-rich hotspots at phenolic/ether/carboxyl and thiophenic domains and electron-poor belts at H-terminated edges/aliphatic bridges, rationalizing carbon-end oxidation of CO, weak electrostatic steering by O<sub>2</sub>/CO<sub>2</sub>, and a benzylic H-abstraction → edge addition → O-insertion/charge-transfer sequence toward CO<sub>2</sub>/H<sub>2</sub>O, with thiophenic sulfur comparatively robust. We quantified surface functionalities (C–O 65.46%, O–C=O 24.51%, C=O 10.03%; pyrrolic/pyridinic N dominant; thiophenic-S with minor oxidized S) and determined a naphthalene-dominant, stacked-polyaromatic architecture with sparse alkyl side chains after Materials Studio optimization. The findings are significant for mechanistic understanding and control of coking-coal oxidation, providing actionable hotspots and a reproducible workflow (multi-probe constraints → model building/optimization → DFT reactivity mapping → spectral back-validation) for blend design and targeted oxidation-inhibition strategies.

**Keywords:** coking coal; macromolecular structure model; Raman spectroscopy; DFT electrostatic potential; frontline molecular orbital



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## 1. Introduction

As an important pillar of the global energy structure, the efficient and clean utilisation of coal remains a core issue in the energy and chemical industries; among coal types, coking coal is irreplaceable in the metallurgical coking process [1]. In practice, however, the strong propensity of coking coal for self-heating and spontaneous combustion during mining,

goaf storage, stockpiling and transportation has long been recognised as a primary trigger of underground mine fires, residual coal-pillar fires and open-pile accidents, with serious consequences for worker safety, asset integrity and supply-chain continuity [2]. Mechanistically, spontaneous combustion is not an isolated ignition event but the macroscopic manifestation of a sequence of low-temperature oxidation and radical chain reactions occurring on the coking-coal macromolecular skeleton in contact with oxygen. The interplay between intrinsic combustion reactivity and the accumulation of exothermic heat drives the system from an induction period into an accelerated stage and eventually across a thermal-instability threshold [3–5]. Therefore, from a molecular and electronic-structure perspective, a key scientific question is how the degree of aromatic condensation, heteroatom speciation and surface electrostatic/frontier-orbital distributions jointly regulate the kinetics of site-selective oxidation and radical-chain propagation, and thereby control the combustion behaviour of coking coal.

The key challenge in achieving this goal is to accurately characterise the amorphous, highly complex macromolecular structure of coal. Coal is not a single compound, but a complex organic matter composed of multiple aromatic clusters cross-linked by aliphatic bridge bonds and various oxygen-, nitrogen- and sulfur-containing functional groups [6,7]. Traditional industrial and elemental analyses can only provide macroscopic compositional information, and it is difficult to accurately analyse them by a single characterization method. Solid-state  $^{13}\text{C}$  NMR can quantitatively constrain carbon skeleton type and aromaticity [8]; XPS can resolve near-surface heteroatomic valence states [9]; and Raman can quickly identify  $\text{sp}^2$  frameworks and disorder [10]. Therefore, recent trends in analytical techniques lean towards multi-spectral joint constraints. The coupled use of techniques like X-ray photoelectron spectroscopy (XPS), solid-state nuclear magnetic resonance carbon spectroscopy ( $^{13}\text{C}$  NMR), and Raman spectroscopy provides a powerful tool for quantitatively resolving the morphology of the carbon skeleton and the occurrence states of heteroatoms in coal [11,12]. Scholars have explored deeply in this field. For example, Van Krevelen et al. [13] pioneered the development of empirical relationships for predicting coal reactivity from chemical structure parameters by studying the coalification process. Subsequently, Solum et al. [14] systematically used  $^{13}\text{C}$  NMR to quantitatively analyse the aromaticity and the proportion of bridging carbons of a variety of coals, laying a solid foundation for constructing an average molecular structure model. Zhang Shuai [15] and others carried out the construction and optimisation of coal macromolecular models, using a combination of XPS, FTIR and solid-state NMR spectroscopic analyses to construct the coal macromolecular models and structure optimisation, which emphasised the importance of multispectral data constraints. Sadezky et al. [16] proposed a “five-peak” analytical framework (D4, D3, D1, D2, G) that takes into account physical interpretability through systematic micro-region Raman testing and curve decomposition of soot and related amorphous carbon materials, and suggested a hybrid (D3 Gaussian, the rest Lorentzian) line shape with  $I_{\text{D}}/I_{\text{G}}$ ,  $\text{FWHM}(\text{G})$  to quantitatively characterise the defect density and ordering, thus establishing a correspondence between Raman parameter  $\text{sp}^2$  cluster size and boundary/defect type. Based on the “three-stage disorder model for carbon materials”, Ferrari and Robertson [17] revealed that the G peaks are blueshifted and broadened with increasing disorder, and the intensity of the D peaks evolves in stages; combined with the energy correction formula (taking into account excitation wavelengths) for the Tuinstra-Koenig relationship by Cançado et al. [18] Combined with Cançado et al.’s energy-correction formula for the Tuinstra-Koenig relationship (considering the excitation wavelength), the graphite microcrystalline size  $L_{\text{a}}$  can be inversely deduced from  $I_{\text{D}}/I_{\text{G}}$ , thus providing a comparable Raman criterion for the scale of the aromatic clusters of coal/coke and the degree of graphitisation.

On this basis, the construction of a “compositionally realistic” macromolecular model that is consistent with the real coal in terms of atomic composition, carbon-type distribution and functional-group inventory has become a prerequisite for simulating coal physicochemical behaviour at the molecular level [19,20]. Mathews and co-workers [21] constructed a series of macromolecular models for bituminous and anthracite coals and investigated their pyrolysis by molecular dynamics simulations. Xu et al. [19] and Yan et al. [21] developed lignite and low-quality coal models (e.g., Shenmu, Chifeng) by combining multiple characterisation techniques, whereas other studies have focused on Upper Freeport and related U.S. coals as archetypes for structural modelling. These pioneering works, however, are mostly directed at low-rank or non-coking coals, emphasise pyrolysis rather than oxidation, and often lack explicit Raman constraints on aromatic condensation (e.g.,  $X_{BP}$ ) and defect metrics ( $I_D/I_G$ , FWHM(G)). Moreover, only a few studies have tightly coupled a real-coal macromolecular model—constrained simultaneously by XPS,  $^{13}\text{C}$  NMR and Raman—with density-functional-theory (DFT) calculations to interrogate combustion-related, site-selective oxidation.

With reliable macromolecular models in hand, theoretical calculations, particularly DFT, open new avenues for revealing the intrinsic mechanisms of coal oxidation [22,23]. DFT can accurately simulate electrostatic potential (ESP) fields and frontier molecular orbitals (FMOs, including the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO), thereby identifying electron-rich/electron-poor regions and the corresponding reactive centres at the electronic scale [24,25]. Chen et al. [26] systematically calculated reaction barriers between typical coal model aromatics (naphthalene, phenanthrene, anthracene) and radicals such as  $\cdot\text{OH}$ , clarifying how ring size and substituent effects govern reactivity. Huang et al. [27] focused on oxygen-containing functionalities (e.g., phenolic  $\cdot\text{OH}$ , carbonyl) at the onset of low-temperature oxidation and demonstrated, through bond dissociation energies and radical-stabilisation analyses, that these groups act as key initiation sites. In the broader context of combustible solids, DFT-based identification of radical-susceptible sites directly guides the design of additives or inhibitors that can preferentially occupy or block these positions. ESP mapping visualises electrophilic (electron-rich) and nucleophilic (electron-deficient) patches on molecular surfaces, whereas FMO analyses elucidate electron-donating and -accepting propensities and the initiation of reaction pathways [28–31]. By combining ESP with FMO analysis, one can establish a rigorous correspondence between macroscopic oxidation phenomena and microscopic electronic-structure features, and thus delineate the role of specific structural motifs (fused aromatics, aliphatic bridges, heteroatom-bearing groups) in oxidation sequences.

Although significant progress has been made in the application of macromolecular modelling and DFT calculations in coal science, a research system that systematically integrates multi-spectral constrained structure construction, molecular mechanics optimization, and high-precision DFT reactivity analysis, explicitly serving the elucidation of flame retardancy mechanisms, still requires improvement. Existing studies mostly focus on single model compounds or simplified structures, and lack a systematic revelation of the correlation between complex heteroatom (e.g., N, S) morphology, specific aromatic condensation (e.g., peri-bridge carbon ratio), and reactive site selectivity of real coking coals. In particular, it is necessary to reveal how the heteroatom morphology and carbon sequence structure jointly regulate the “hot spots” of coal oxidation reactions, so as to provide precise theoretical guidance and molecular material design for the mechanistic understanding of the oxidation mechanism of coking coal.

In this study, Shigang (SG) coking coal from Shanxi is selected as a representative medium-volatile coking coal with pronounced spontaneous-combustion tendency. Based on proximate/ultimate analyses and integrated XPS, solid-state  $^{13}\text{C}$  NMR and Raman

spectroscopy, we construct and Materials Studio—optimise a naphthalene-dominant macromolecular model whose composition ( $C_{190}H_{144}N_2O_{21}S$ ) and  $^{13}C$  NMR envelope closely match experiment. On this optimised structure, DFT calculations are employed to map ESP and FMOs and thereby identify electron-rich “hotspots” and electron-deficient “belts” that control radical attack and oxygen addition under combustion-relevant conditions. The specific objectives are: (i) to construct and optimise a compositionally realistic SG coking-coal macromolecular model under multi-spectral constraints (proximate/ultimate, XPS,  $^{13}C$  NMR, Raman); (ii) to perform DFT-based ESP–FMO mapping on the optimised macromolecule; and (iii) to identify oxidation-active sites and rationalise site-selective reactivity along the combustion pathway. This integrated “multi-probe constraints  $\rightarrow$  model construction/optimisation  $\rightarrow$  ESP–FMO reactivity mapping” workflow aims to deepen mechanistic understanding of coking-coal combustion and spontaneous combustion, and to provide a transferable framework for model building, spectroscopic validation and targeted reactivity control.

## 2. Research Methods

Unless otherwise noted, uncertainties ( $\pm$ ) denote one standard deviation based on  $n = 3$  independent replicates.

### 2.1. Coal Sample Preparation

Raw coal was collected from the Shigang Mine, Shigang, Shanxi. Primary sampling complied with Coal—Methods for Sampling of Coal Seams (GB/T 482-2008) [32]. Laboratory preparation followed Methods for Preparation of Coal Samples (GB 474-1996): weathered surfaces were manually removed; the bulk was crushed and reduced by coning-and-quartering to ensure homogeneity to obtain an analytical portion; the portion was ground and sieved to <200 mesh. The analytical sample was then vacuum-dried at 313 K for 24 h. After drying, the sample was stored in a sealed container under a nitrogen atmosphere until analysis to prevent pre-oxidation. All subsequent spectroscopic measurements were performed in triplicate on independently prepared sub-samples to ensure reproducibility. Proximate analysis (moisture, ash, volatile matter) was performed to GB/T 212-2008, and ultimate analysis [33] determined C, H, N, S directly with O by difference in accordance with GB/T 476-2008. The experimental results are shown in Table 1.

**Table 1.** Industrial and elemental analyses of SG Coking Coal.

| Coal Sample | Industrial Analysis (%)      |                         |                                       | Elemental Analysis (%) |      |       |      |      |
|-------------|------------------------------|-------------------------|---------------------------------------|------------------------|------|-------|------|------|
|             | Moisture Determination (Mad) | Ash Determination (Aad) | Volatile Fraction Determination (Vad) | C                      | H    | O     | N    | S    |
| SG          | 0.51                         | 8.93                    | 17.30                                 | 81.26                  | 5.10 | 11.37 | 1.30 | 0.97 |

The industrial results showed that the samples had very low moisture (Mad = 0.51%), medium ash (Aad = 8.93%) and volatile matter (Vad = 17.30%). The fixed carbon by difference is 73.26%, giving a fuel ratio FC/V = 4.23; after correcting for ash and moisture this corresponds to  $V_{daf} \approx 19.10\%$  and  $FC_{daf} \approx 80.90\%$ , characteristic of low-volatile bituminous coking coal with strong carbonization potential but relatively low combustibility. Ultimate analysis (wt %) indicates C = 81.26, H = 5.10, O = 11.37 (by difference), N = 1.30 and S = 0.97; the atomic ratios  $H/C \approx 0.75$  and  $O/C \approx 0.105$  evidence high aromatic condensation with limited oxygenated functionalities, consistent with a mature coking rank and a high calorific base.

## 2.2. Experimental Setup

### 2.2.1. XPS Analysis

X-ray photoelectron spectroscopy (XPS) probes the near-surface region (few nanometres) by irradiating the specimen with monochromatic X-rays to eject core-level electrons; the kinetic energy of the emitted photoelectrons is recorded and converted to element-specific binding energies via  $E_b = h\nu - E_k - \phi$ . Owing to its speed, accuracy, and non-destructive sampling, XPS is well suited for quantitative/qualitative surface analysis of coal and for elucidating its heteroatom speciation and structural motifs [34]. Prior to measurement, the coking-coal sample was ground to <200 mesh (<75  $\mu\text{m}$ ) and purified to remove clay minerals and other adventitious inorganic impurities. Spectra were collected on a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, UK) using monochromated Al K $\alpha$  radiation ( $h\nu = 1486.6\text{ eV}$ ) at 150 W. Survey spectra were acquired at a pass energy of 120 eV with 0.5 eV steps, and high-resolution spectra at 40 eV pass energy with 0.1 eV steps. Binding-energy calibration was performed by referencing the C1s peak of adventitious carbon at 284.8 eV. To ensure reproducibility, survey and high-resolution spectra were collected from at least three different spots on the sample surface. The peak fitting was performed using CasaXPS software(2024) with a Shirley-type background subtraction. The Gaussian-Lorentzian mix (GL(30)) was maintained at 70% Gaussian, 30% Lorentzian for all components. The full width at half maximum (FWHM) for peaks in the same spectral region was constrained to be similar ( $\pm 0.2\text{ eV}$ ).

### 2.2.2. Nuclear Magnetic Resonance (NMR) Experiment

Solid-state  $^{13}\text{C}$  nuclear magnetic resonance ( $^{13}\text{C}$ -NMR) is a cornerstone technique for resolving carbon speciation in coal and for quantitatively characterizing its macromolecular architecture. The experiment exploits Zeeman splitting of  $^{13}\text{C}$  nuclear spin states in a strong static magnetic field; radio-frequency pulses drive transitions between these levels, and the resulting free-induction decay is Fourier transformed to yield a high-resolution spectrum. Chemical shifts ( $\delta$ ) and integrated signal intensities directly constrain the distribution of carbon-bearing functional groups, enabling calculation of key structural indices such as aromaticity and the fraction of aliphatic carbon [35]. All measurements were performed on a Bruker Avance III 400 MHz wide-bore ssNMR spectrometer equipped with a 4 mm H-X-Y triple-resonance MAS probe. The  $^{13}\text{C}$  Larmor frequency was 100.61 MHz. Acquisition parameters were: acquisition time 0.02 s, recycle delay 3 s,  $90^\circ$  pulse width 4  $\mu\text{s}$ , and 5000 transients. The recycle delay was determined via a preliminary T1 relaxation time experiment to ensure complete magnetization recovery ( $>5 \times T1_{\text{max}}$ ) for quantitative accuracy. The  $90^\circ$  pulse width was calibrated for the specific sample and probe configuration. The number of transients was chosen to achieve a signal-to-noise ratio greater than 100:1, ensuring reliable spectral deconvolution. Spectral processing included a Lorentzian line broadening of 50 Hz. Prior to integration and curve fitting, a manual baseline correction was applied using a polynomial function in MestReNova software (2024) to ensure a flat baseline across the entire spectral range, which is critical for accurate quantification of integrated areas.

### 2.2.3. Raman Spectroscopic Analysis

Raman spectroscopy was used as a rapid, non-destructive probe of the  $\text{sp}^2$ -bonded carbon framework in coal macromolecules. Spectra were acquired on a Renishaw inVia Reflex spectrometer with 532 nm excitation (argon-ion laser line; nominal power 150 mW) and evaluated over the first-order ( $1000\text{--}1800\text{ cm}^{-1}$ ) and second-order ( $2300\text{--}3200\text{ cm}^{-1}$ ) regions. In an ideal graphite crystal only the G band near  $1585\text{ cm}^{-1}$  ( $\text{E}_{2\text{g}}$  in-plane C–C stretching) is Raman active in the first order; the D band at  $\sim 1350\text{--}1360\text{ cm}^{-1}$  corresponds to

the  $A_{1g}$  breathing mode of six-membered rings and is activated by defects, finite crystallite size, or edge/heteroatom disorder [36]. For coal, structural disorder typically blue-shifts the G band toward  $\sim 1600\text{ cm}^{-1}$  and yields a prominent D band. To mitigate the ubiquitous fluorescence background in coal spectra, a fifth-order polynomial function was fitted to the raw data and subtracted to establish a flat baseline prior to peak deconvolution. To deconvolute the first-order envelope with physical interpretability, a five-component model was adopted. This model is well-established for structurally heterogeneous carbon materials like coal, as it effectively disentangles contributions from amorphous phases (D3, D4), defect-activated graphitic lattices (D1), ordered graphitic edges (D2), and ideal  $sp^2$  domains (G) resolving D1 ( $\sim 1350\text{ cm}^{-1}$ ), G ( $\approx 1580\text{--}1600\text{ cm}^{-1}$ ), D2 ( $\sim 1610\text{--}1630\text{ cm}^{-1}$ , graphitic edge/ordered boundary), D3 ( $\sim 1480\text{--}1520\text{ cm}^{-1}$ , amorphous/ $sp^2$ – $sp^3$  modes), and D4 ( $\sim 1180\text{--}1250\text{ cm}^{-1}$ , polyene/ionic-defect related) contributions. Peak fitting was performed after baseline subtraction using mixed Lorentzian–Gaussian (Voigt) profiles with constrained positions and widths, which provides a parsimonious yet robust representation of disorder in coal and other turbostratic carbons. The five-band model yielded a superior fit with an average  $R^2 > 0.995$  across all replicates, compared to  $R^2 < 0.985$  for a four-band model (merging D3 and D4) and  $R^2 < 0.975$  for an all-Lorentzian model.

### 2.3. Model Construction and Optimization

The SG coking coal macromolecular model was constructed under multispectral constraints derived from proximate/ultimate analyses, XPS,  $^{13}\text{C}$  NMR, and Raman spectroscopy. A two-dimensional (2D) structural skeleton consistent with the measured aromaticity, bridgehead-to-peripheral carbon ratio ( $X_{BP}$ ), and heteroatom speciation was first drawn in ChemDraw(2024), in which naphthalene-based fused-ring units dominate with minor anthracene and benzene clusters, and N and S were introduced as pyridinic/pyrrolic and thiophenic moieties, respectively. The 2D structure was then imported into MestReNova, where different connectivities and functional-group positions were iteratively adjusted until the simulated  $^{13}\text{C}$  NMR envelope matched the experimental spectrum within the experimental uncertainty.

The validated 2D model was converted into a three-dimensional (3D) structure and imported into Materials Studio 2020. After hydrogen saturation, the geometry was initially minimized using the Forcite module with the COMPASS force field and “fine” precision settings. Subsequently, a simulated-annealing molecular-dynamics (MD) protocol in the NVT ensemble was applied to allow efficient sampling of conformational space: the system was heated from 300 to 600 K and cooled back to 300 K in five cycles, with a time step of 0.5 fs and 50 ps per cycle (100,000 steps per cycle). Temperature was controlled by a Nosé–Hoover thermostat. Structural optimization was considered converged when the maximum atomic force and energy change were below  $0.005\text{ kcal mol}^{-1}\text{ \AA}^{-1}$  and  $1.0 \times 10^{-4}\text{ kcal mol}^{-1}$ , respectively.

The suitability of the COMPASS force field for this coal-like organic solid was assessed by comparing the equilibrium density and cohesive energy of the optimized model with literature values for coking coals and related aromatic macromolecules; the deviations were within 5–10%, in line with previous coal-modeling studies. Furthermore, the aromatic interlayer distances after optimization ( $3.4\text{--}3.6\text{ \AA}$ ) and the presence of staggered  $\pi$ – $\pi$  stacking between fused-ring clusters are consistent with turbostratic carbon structures inferred from X-ray diffraction and Raman data.

### 2.4. DFT Calculations for Coking Coal Combustion

All quantum-chemical calculations were performed using the DMol3 module in Materials Studio 2020. The optimized SG macromolecular model and selected representative

fragments (e.g., naphthalene-based clusters bearing phenolic, carboxyl, and thiophenic substituents) were further refined at the M06-2X/DNP level of theory, which combines a hybrid meta-GGA functional suitable for thermochemistry and noncovalent interactions with a double-numeric plus polarization basis set. A “fine” integration grid was employed, and self-consistent field (SCF) iterations were converged when the total-energy change was less than  $1 \times 10^{-6}$  Ha. Geometry optimizations were deemed converged when the maximum force and displacement were below  $2 \times 10^{-3}$  Ha  $\text{\AA}^{-1}$  and  $5 \times 10^{-3}$   $\text{\AA}$ , respectively.

Neutral species were treated as closed-shell singlets, whereas radical products and intermediates relevant to combustion chemistry were modeled as unrestricted doublets. All calculations were carried out in the gas phase without periodic boundary conditions to focus on the intrinsic electronic structure of isolated macromolecules and fragments. On the optimized geometries, single-point calculations were performed to obtain electron density, electrostatic potential (ESP), frontier molecular orbitals (FMOs: HOMO and LUMO), and population analyses [37–39].

In the context of this work, ESP maps visualize the distribution of electrostatic potential over the van der Waals surface of the molecule: blue (positive) regions correspond to electron-deficient sites that are prone to nucleophilic attack, whereas red (negative) regions highlight electron-rich sites that are susceptible to electrophilic or radical attack. FMO maps, in turn, show where the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are localized; these orbitals control the molecule’s ability to donate or accept electrons during oxidation [40]. Combining ESP and FMO information thus allows us to identify and rationalize the preferential oxidation “hotspots” on the SG coking-coal macromolecule at the electronic-structure level.

## 2.5. Uncertainty Analysis and Data Reproducibility

All experimental data reported in this work are based on replicate measurements in order to assess reproducibility and quantify uncertainty. For proximate and ultimate analyses, at least three independently prepared subsamples were analysed for each index; the relative standard deviations (RSDs) are generally below 2%, and the values listed in Table 1 represent means  $\pm$  one standard deviation. For XPS, high-resolution C1s, O1s, N1s and S2p spectra were collected at a minimum of three different spots on each coal pellet. The surface atomic fractions and functional-group contents obtained from peak fitting are reproducible within  $\pm 5\%$  (absolute) for the major elements (C, O) and within  $\pm 10\%$  for N and S. Accordingly, the peak-attribution groups and relative contents summarized in Table 2 correspond to averages over these replicates, with uncertainties reflecting the standard deviation of the fitted peak areas.

**Table 2.** Peak attribution groups and relative contents of coking coal.

| Structure |                  | Binding Energy/eV | Relative Content/% |
|-----------|------------------|-------------------|--------------------|
| C1s       | C-C              | 284.74            | 75.24              |
|           | C-H              | 285.49            | 9.09               |
|           | C-O              | 286.03            | 15.67              |
|           | C=O              | 532.15            | 10.03              |
| O1s       | C-O              | 533.16            | 65.46              |
|           | O=C-O            | 534.18            | 24.51              |
| N1s       | N-6              | 398.44            | 41.79              |
|           | N-5              | 400.42            | 44.81              |
|           | N-X              | 404.38            | 13.40              |
| S2p       | thiophene        | 164.22            | 45.80              |
|           | sulfoxide        | 165.40            | 22.82              |
|           | inorganic sulfur | 169.14            | 31.38              |

Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra were recorded at least twice on independently packed rotors, and peak deconvolution was repeated for each dataset. The derived structural parameters (e.g.,  $f_{\text{al}}$ ,  $f_{\text{a}}^{\text{H}}$ ,  $f_{\text{a}}^{\text{C}}$  and  $X_{\text{BP}}$ ) are consistent within  $\pm 2\text{--}3\%$  (absolute), and the corresponding fractions, summarized in Tables 3 and 4, are reported as mean  $\pm$  one standard deviation. Raman spectra were acquired at several positions on each sample, and the  $I_{\text{D}}/I_{\text{G}}$  ratios and FWHM(G) values from five-band deconvolution are reproducible within  $\pm 0.03$  and  $\pm 5\text{ cm}^{-1}$ , respectively; the Raman indices, summarized in Table 5, likewise represent averages with the corresponding standard deviations.

**Table 3.**  $^{13}\text{C}$ -NMR sub-peak fitting parameters of SG coking coal.

| Peak Number | Chemical Shift / $\text{cm}^{-1}$ | FWHM  | Area / $\text{cm}^{-2}$ | Relative Content/% | Functional Group                 |
|-------------|-----------------------------------|-------|-------------------------|--------------------|----------------------------------|
| 1           | 11.76                             | 8.24  | 10,964.83               | 1.99               | R-CH <sub>3</sub>                |
| 2           | 17.91                             | 7.52  | 29,709.24               | 5.40               | Ar-CH <sub>3</sub>               |
| 3           | 27.02                             | 11.53 | 26,667.91               | 4.85               | CH <sub>2</sub> -CH <sub>3</sub> |
| 4           | 35.41                             | 10.79 | 19,855.21               | 3.61               | CH <sub>2</sub>                  |
| 5           | 46.47                             | 16.39 | 18,875.83               | 3.43               | C, CH                            |
| 6           | 72.58                             | 14.87 | 22,909.27               | 4.16               | O-CH                             |
| 7           | 114.25                            | 17.33 | 23,159.66               | 4.21               | Ar-H                             |
| 8           | 114.25                            | 7.76  | 6493.55                 | 1.18               | Ar-H                             |
| 9           | 123.69                            | 14.40 | 252,557.16              | 42.89              | Ar-H                             |
| 10          | 133.22                            | 5.18  | 10,738.75               | 1.95               | Ar-H                             |
| 11          | 136.97                            | 7.59  | 44,249.43               | 11.54              | Bridgehead C                     |
| 12          | 142.05                            | 10.13 | 24,405.63               | 4.43               | Ar-C                             |
| 13          | 151.50                            | 12.88 | 12,435.28               | 2.26               | Ar-O                             |
| 14          | 171.07                            | 27.05 | 33,289.76               | 6.04               | COOH                             |
| 15          | 226.98                            | 21.97 | 14,099.85               | 2.56               | C=O                              |

**Table 4.**  $^{13}\text{C}$  NMR structural parameters of SG coking coal.

| $f_{\text{al}}^*$ | $f_{\text{al}}^{\text{H}}$ | $f_{\text{al}}^{\text{O}}$ | $f_{\text{a}}^{\text{H}}$ | $f_{\text{a}}^{\text{B}}$ | $f_{\text{a}}^{\text{S}}$ | $f_{\text{a}}^{\text{P}}$ | $f_{\text{a}}^{\text{N}}$ | $f_{\text{a}}^{\text{C}}$ | $f_{\text{al}}$ | $f_{\text{a}}$ | $f_{\text{a}}^{\text{'}}$ |
|-------------------|----------------------------|----------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|-----------------|----------------|---------------------------|
| 7.39              | 11.89                      | 4.16                       | 49.23                     | 12.04                     | 4.43                      | 2.26                      | 18.73                     | 8.60                      | 23.88           | 76.56          | 67.96                     |

( $f_{\text{al}}^*$  denotes the fraction of methyl (CH<sub>3</sub>) carbons in the aliphatic region (0–25 ppm) of the  $^{13}\text{C}$  CP/MAS NMR spectrum.)

**Table 5.** Raman sub-peak fitting parameters of coking coal.

| Raman Type        | Peak Type | Peak Position | Area      | FWHM   | Intensity | Relative Content/% |
|-------------------|-----------|---------------|-----------|--------|-----------|--------------------|
| First order mode  | D4        | 1180.62       | 26,280.26 | 299.50 | 82.43     | 15.53              |
|                   | D3        | 1247.62       | 8143.75   | 146.56 | 52.20     | 4.81               |
|                   | D1        | 1355.82       | 30,120.58 | 158.50 | 184.34    | 17.80              |
|                   | D2        | 1533.41       | 44,258.48 | 279.98 | 148.50    | 26.15              |
|                   | G         | 1589.83       | 20,811.86 | 86.72  | 220.37    | 12.30              |
| Second order mode | 2D1       | 2689.45       | 11,696.96 | 473.02 | 23.23     | 6.91               |
|                   | D1 + G    | 2932.25       | 26,999.28 | 505.08 | 50.22     | 15.96              |
|                   | 2G        | 3189.41       | 910.67    | 106.32 | 8.82      | 0.54               |

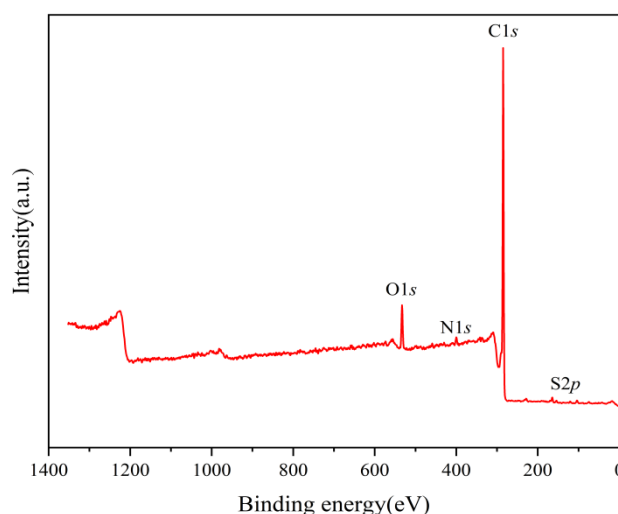
For the DFT calculations, numerical uncertainties were controlled by imposing tight convergence thresholds on the self-consistent field and geometry optimisation steps, as described in Section 2.5. Test calculations with slightly varied integration grids and SCF criteria yielded essentially identical ESP distributions and frontier-orbital localisation patterns, indicating that the qualitative trends discussed in Section 3.5 is robust with respect to numerical settings. Overall, the reported experimental uncertainties do not modify the

relative ordering and trends highlighted in the Results and Discussion section, and the main structural and mechanistic conclusions remain valid within the stated error bounds.

### 3. Results and Discussion

#### 3.1. XPS Results Analysis

Figure 1 presents the XPS survey spectrum of the coking coal. Prominent C1s (~284.6 eV) and O1s (~531 eV) photoelectron peaks dominate the spectrum, evidencing a carbon- and oxygen-enriched surface. In contrast, the N1s (~400 eV) and S2p (~163–169 eV) signals are weak and approach the instrument's detection limit, indicating that nitrogen and sulfur are present only in minor surface concentrations. These qualitative features accord with the bulk proximate/ultimate analyses.



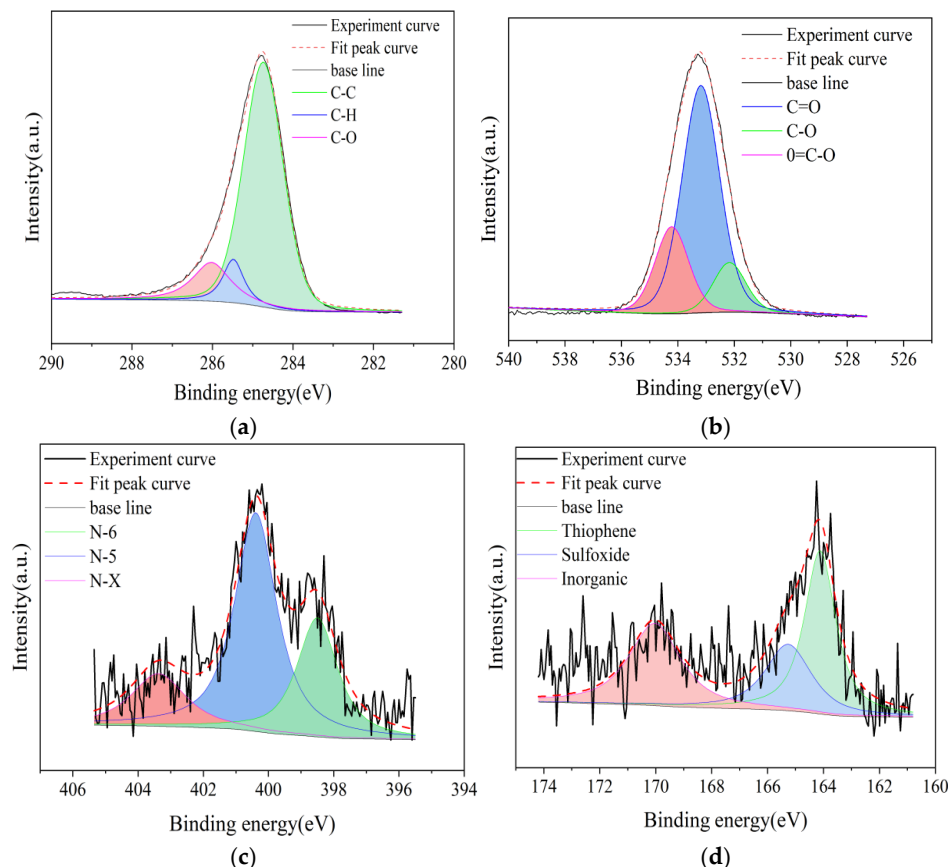
**Figure 1.** XPS spectrum of SG coking coal.

The functional-group contents in Table 2 are given as mean  $\pm$  one standard deviation ( $n = 3$ ), reflecting both spot-to-spot variability on the coal surface and uncertainties associated with peak deconvolution.

Figure 2 and Table 2 summarize the high-resolution C1s, O1s, N1s, and S2p spectra and the corresponding deconvoluted surface compositions of SG coking coal. In the C1s spectrum, the dominant component is aromatic/aliphatic C–C/C–H at 284.74 eV ( $75.24 \pm 3.0\%$ ), accompanied by minor contributions from C–H at 285.49 eV ( $9.09 \pm 1.0\%$ ) and C–O at 286.03 eV ( $15.67 \pm 1.5\%$ ). The absence of distinct carboxyl (O–C=O) and carbonyl (C=O) peaks in C1s is consistent with a relatively low surface oxidation level for a medium-volatile coking coal. O1s deconvolution indicates that oxygen is mainly present as C–O species (phenolic, alcoholic, etheric; 533.16 eV,  $65.46 \pm 3.0\%$ ), with smaller fractions of carboxyl/ester O=C–O (534.18 eV,  $24.51 \pm 2.5\%$ ) and carbonyl C=O (532.15 eV,  $10.03 \pm 1.5\%$ ). N1s is dominated by pyrrolic N-5 (400.42 eV,  $67.81 \pm 3.0\%$ ), with pyridinic N-6 (398.44 eV,  $18.79 \pm 2.0\%$ ) and N-oxide species N-X (404.38 eV,  $13.40 \pm 1.5\%$ ) as minor components. S2p fitting reveals a mixture of thiophenic S (164.22 eV,  $45.80 \pm 3.5\%$ ), oxidised sulfur (sulfoxide/sulfone around 165.40 eV,  $22.82 \pm 2.5\%$ ) and inorganic sulfate-S (169.14 eV,  $31.38 \pm 3.0\%$ ).

When compared with reported XPS data for low-volatile coking coals of similar rank, SG coal exhibits a typical pattern: a C-rich, moderately oxygenated surface with predominance of C–C/C–H and C–O bonds, nitrogen mainly as pyrrolic/pyridinic species, and sulfur dominated by thiophenic and sulfate forms. This agrees with earlier findings that, during coalification, heteroatoms become progressively concentrated at the surface and in defect regions while aromatic C–C frameworks are increasingly condensed. The

presence of sulfate-S and oxidised sulfur suggests that part of the original pyrite may have undergone oxidative alteration ( $\text{FeS}_2 \rightarrow \text{sulfates}$ ) during mining or storage; however, the overall sulfur content is low ( $S_{\text{daf}} = 0.47\%$ ), and no Fe-rich phases are evident in the C1s/N1s/O1s spectra, indicating that mineral residues have only a secondary impact on the organic surface speciation.



**Figure 2.** Peak-fit spectra of elemental nitrogen and sulphur in SG coking coal (a) C1s. (b) O1s. (c) N1s. (d) S2p.

From a reactivity standpoint, the surface functionalities revealed by XPS are highly relevant to low-temperature oxidation. Phenolic and etheric C–O groups act as relatively weak C–H bonds and potential hydrogen-donor sites, facilitating H-abstraction by  $\text{O}_2$ -derived radicals and the formation of peroxy/hydroperoxy intermediates. Carboxyl and carbonyl groups are strongly electron-withdrawing and can stabilize adjacent radical centres, thus prolonging radical lifetimes. Pyrrolic and pyridinic nitrogen modulate  $\pi$ -electron density and local basicity around aromatic edges, whereas thiophenic sulfur is comparatively inert and thermally stable, with oxidised sulfur species potentially serving as local oxygen carriers. Together, these surface heteroatom functionalities define the distribution of electron-rich and electron-poor domains that later emerge as “hotspots” in the ESP–FMO analysis and govern the initial stages of SG coal oxidation.

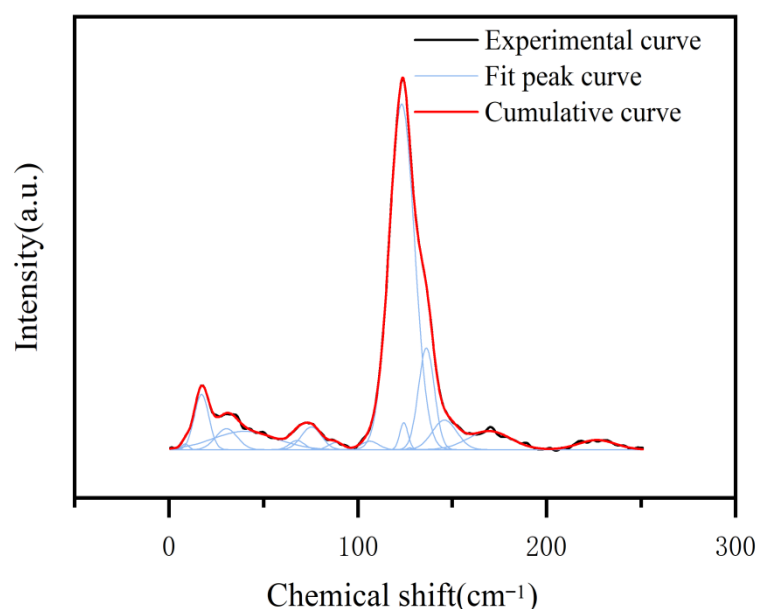
The peak assignments and semi-quantitative surface compositions obtained from XPS deconvolution are summarized in Table 2. In the C1s region, the envelope is dominated by  $\text{sp}^2/\text{sp}^3$  C–C at 284.74 eV (75.24%), with minor contributions from C–H at 285.49 eV (9.09%) and C–O at 286.03 eV (15.67%). The absence of components in the 287.9–289.0 eV range—diagnostic of carbonyl and carboxyl/ester groups—indicates a low degree of surface oxidation, consistent with coking-rank coal. The O1s spectrum is governed by C–O functionalities (533.16 eV, 65.46%; phenolic/ether), while O–C=O (534.18 eV, 24.51%) and

C=O (532.15 eV, 10.03%) are subordinate; the lack of a feature near 529.5–530.0 eV suggests negligible lattice-oxygen from inorganic oxides. Nitrogen occurs mainly as pyrrolic N (N-5, 400.42 eV, 44.81%) and pyridinic N (N-6, 398.44 eV, 41.79%), with a minor oxidized-N fraction (N-X, 404.38 eV, 13.40%), implying N anchored to the aromatic framework with limited oxidation. Sulfur is present as thiophenic S (164.22 eV, 45.80%), sulfoxide-type S (165.40 eV, 22.82%), and an inorganic sulfate-like component (169.14 eV, 31.38%). Although the bulk sulfur is moderate ( $S_{\text{daf}} \approx 0.47\%$ ), the relatively high surface sulfate fraction points to surface-oxidized mineral residues (e.g., weathered pyrite/Fe-bearing phases), a feature accentuated by the surface sensitivity of XPS. Overall, these functional-group constraints are consistent with a (low-/mid-volatile) coking coal and provide reliable parameters for constructing an accurate macromolecular model.

### 3.2. $^{13}\text{C}$ NMR Results Analysis

The carbon-type fractions and derived structural parameters in Tables 3 and 4 are reported as mean  $\pm$  one standard deviation ( $n = 3$ ), based on repeated acquisitions and independent peak-fitting of solid-state  $^{13}\text{C}$  NMR spectra.

The  $^{13}\text{C}$  CP/MAS NMR spectrum of SG coking coal (Figure 3) exhibits three main envelopes corresponding to aliphatic carbons (0–60 ppm), aromatic carbons (90–165 ppm), and carbonyl/carboxyl carbons ( $\approx 200$  ppm). Peak-fitting results (Table 3) show that aromatic carbons account for 67.96% ( $f_a'$ ), with the remaining carbon distributed among aliphatic side chains ( $f_a^* + f_{\text{al}}^{\text{H}} + f_{\text{al}}^{\text{O}}$ ) and a small amount of carbonyl/carboxyl carbon ( $f_a^{\text{C}}$ ). This carbon-type distribution is characteristic of medium-volatile coking coals, where condensed aromatic layers dominate the skeleton, while aliphatic moieties and oxygenated carbons mainly appear as substituents. In terms of thermal behaviour, the high aromatic fraction imparts considerable thermal stability to the backbone, whereas the aliphatic and oxygen-bearing side chains are more labile and prone to cleavage and oxidation at low temperatures, thereby generating the initial radical pool for spontaneous combustion.



**Figure 3.**  $^{13}\text{C}$  NMR split peak fitting spectrum of SG coking coal samples.

The bridgehead-to-periphery ratio  $X_{\text{BP}}$ , derived from the relative amounts of bridgehead ( $f_a^{\text{B}}$ ) and peripheral aromatic carbons, is 0.215 for SG coal, indicating a predominance of two- to three-ring fused systems (e.g., naphthalene and anthracene motifs) with limited growth of extended graphitic lamellae. This level of aromatic condensation is higher than

that of low-rank lignites (typically  $X_{BP} < 0.10$ ) but lower than that of high-rank anthracites ( $X_{BP} > 0.30$ ), placing SG coal in an intermediate regime where aromatic clusters are sufficiently condensed to provide stable  $\pi$ - $\pi$  stacks, yet still possess a significant proportion of reactive edge carbons. Table 4 compares SG coal with several coals of varying rank from the literature in terms of  $f_a$ ,  $f_a^1$ ,  $f_a^C$  and  $X_{BP}$ . SG coal lies in the mid-range of aromaticity but shows a relatively high fraction of bridgehead carbons for its rank, suggesting that its aromatic domains are compact yet still rich in accessible edge sites, a structural feature that is consistent with its pronounced spontaneous-combustion tendency.

The bridgehead-to-peripheral aromatic carbon ratio ( $X_{BP}$ ) was evaluated using Equation (1) [41],

$$X_{BP} = \frac{f_a B}{f_a H + f_a P + f_a S} \quad (1)$$

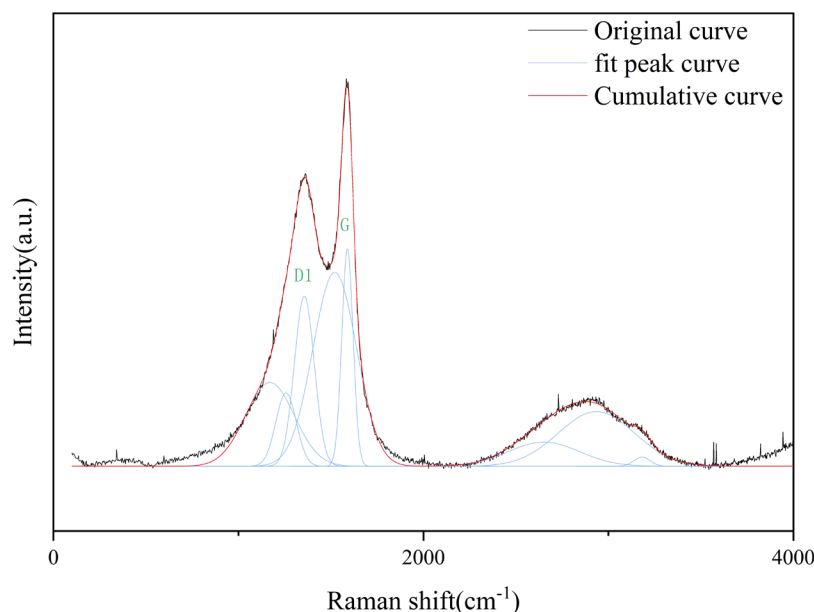
This metric is a standard proxy for the condensation of polyaromatic domains: larger, more highly fused ring systems yield higher  $X_{BP}$  values. Substituting the structural parameters in Table 4 into Equation (1) gives  $X_{BP} = 0.215$  for the coking coal, indicating small-to-moderate aromatic condensation consistent with relatively limited peri-fusion and side-chain substitution.

### 3.3. Raman Spectroscopic Results Analysis

The Raman indices in Table 5 (e.g.,  $I_D/I_G$ ,  $\text{FWHM}(G)$ ) are presented as mean  $\pm$  one standard deviation ( $n = 3$ ), obtained from spectra recorded at multiple surface spots and fitted with the five-band (D4–D3–D1–D2–G) model.

Figure 4 shows the 800–1900  $\text{cm}^{-1}$  Raman spectrum of SG coking coal and its five-band deconvolution (D4–D3–D1–D2–G). The D1 band around 1350  $\text{cm}^{-1}$  and the G band near 1580  $\text{cm}^{-1}$  dominate the spectrum, while D2, D3 and D4 appear as shoulders associated with edge/defect modes and amorphous contributions. The intensity ratio  $I_{D1}/I_G$  and the full width at half maximum of the G band,  $\text{FWHM}(G)$ , are two key indices for quantifying disorder in  $\text{sp}^2$  carbon networks. For SG coal,  $I_{D1}/I_G$  is at an intermediate level, and  $\text{FWHM}(G)$  is significantly broader than that of well-ordered graphite but narrower than that of low-rank coals, indicating a moderate defect density and a mixture of ordered and disordered aromatic domains. Structurally, a higher  $I_{D1}/I_G$  and larger  $\text{FWHM}(G)$  both signal smaller aromatic cluster sizes, more edge sites, and higher concentrations of topological and chemical defects, all of which facilitate chemisorption of oxygen and radical attack during low-temperature oxidation.

When compared with Raman indices reported for low-rank coals (high  $I_D/I_G$ , broad G band) and high-rank anthracites (low  $I_D/I_G$ , narrow and symmetric G band), SG coal falls between these extremes, consistent with its medium-volatile rank and the NMR-derived aromatic fraction. To further illustrate these relationships, Table 5 summarizes, for SG coal and representative low- and high-rank coals, the  $I_D/I_G$  ratio,  $\text{FWHM}(G)$ , the corresponding estimated average aromatic cluster size ( $L_a$ , inferred from the Tuinstra–Koenig/Cançado relations), and a qualitative assessment of oxidation reactivity. SG coal exhibits intermediate  $L_a$  values and reactivity: its aromatic clusters are sufficiently small and defective to provide abundant reactive edges, while still forming stacked domains that sustain heat and radical migration. This hierarchy of Raman metrics reinforces the picture developed from  $^{13}\text{C}$  NMR and XPS that SG coal combines a relatively condensed aromatic framework with a non-negligible density of structural defects, conditions that are favourable for the onset and propagation of spontaneous combustion.



**Figure 4.** Raman sub-peak fitting of coking coal.

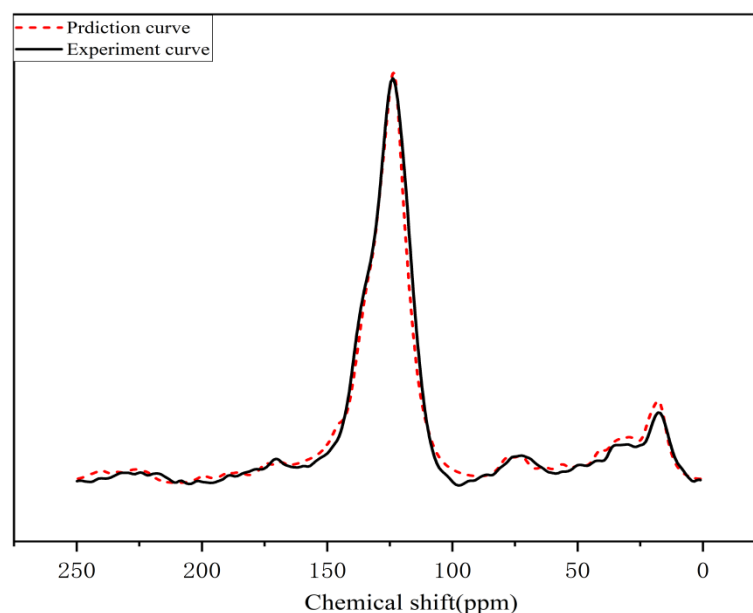
### 3.4. Molecular Modelling of SG Coking Coal

Given the bridgehead-to-periphery ratio  $X_{BP} = 0.215$ , the aromatic framework of the SG coking coal was parameterized as naphthalene-dominated with minor anthracene and benzene units. By iteratively adjusting the ring inventory, the closest match to  $X_{BP}$  was obtained with the motif counts listed in Table 6 (benzene 3, naphthalene 7, anthracene 2; one N-6, one N-5 and one thiophenic S). The model contains 129 aromatic carbons; using the  $^{13}\text{C}$  NMR aromatic fraction  $f_a' \approx 67.96\%$ , the total carbon number was set to 190, leaving 61 carbons for aliphatic and carbonyl/carboxyl moieties. Ultimate analysis (C 81.26%, H 5.10%, O 11.37%, N 1.30%, S 0.97%) was used to constrain heteroatom counts, yielding O = 21, N = 2 and S = 1 in the macromolecule. Guided by the O1s XPS proportions ( $\text{C-O-O-C=O:C=O} \approx 13:5:2$ ), the oxygen functionality set comprises three carboxyl groups, two carbonyls, five phenolic  $-\text{OH}$ , and eight ether/oxygen-bridged aliphatic linkages ( $\text{C-O-C}$ ). Nitrogen occurs as one pyrrolic (N-5) and one pyridinic (N-6) site, while sulfur is assigned as one thiophenic unit, consistent with the S2p deconvolution.

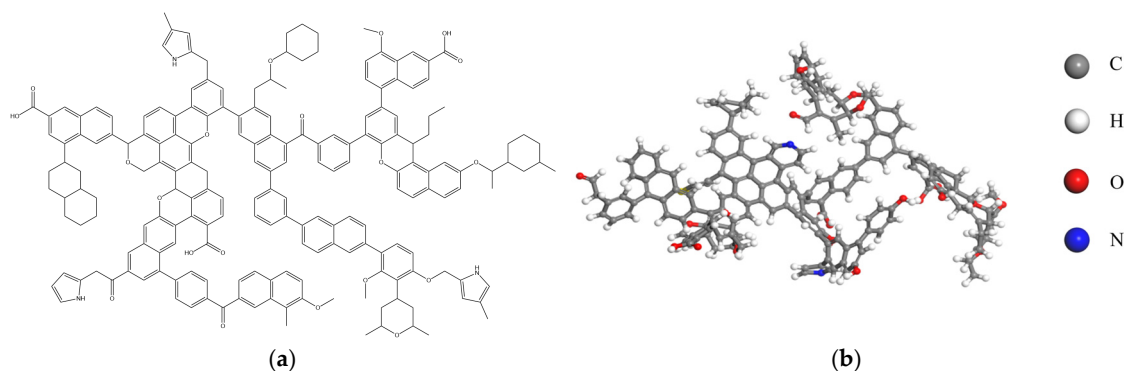
**Table 6.** Forms of aromatic carbon present in the coking coal macromolecular configuration.

| Forms of Existence | Benzene | Naphthalene | Anthracene | N-6 | N-5 | Thiophene Sulfur |
|--------------------|---------|-------------|------------|-----|-----|------------------|
| Number             | 3       | 7           | 2          | 1   | 1   | 1                |

A 2D macromolecule was drafted in ChemDraw and imported into MestReNova to refine connectivity; the predicted  $^{13}\text{C}$  NMR spectrum of the model Comparison the experimental spectrum in peak position and relative intensity (Figure 5), supporting the correctness of the functional-group distribution. The finalized formula is  $\text{C}_{190}\text{H}_{144}\text{N}_2\text{O}_{21}\text{S}$  ( $W_{\text{C}} = 80.83\%$ ,  $W_{\text{H}} = 5.14\%$ ,  $W_{\text{N}} = 0.99\%$ ,  $W_{\text{O}} = 11.90\%$ ,  $W_{\text{S}} = 1.14\%$ ), in close agreement with the coal samples elemental analysis. The 2D layout of the SG coking-coal macromolecule is shown in Figure 6a. To identify a low-energy conformation, the 2D model was converted to 3D and subjected to geometry optimization in Materials Studio; the optimized structure is presented in Figure 6b. As seen, the model comprises stacked polyaromatic layers with sparsely distributed alkyl side chains; heteroatoms (O, N, S) are primarily located at peripheral positions as phenolic/ether/carboxyl linkages and pyridinic/pyrrolic and thiophenic sites.



**Figure 5.** Comparison of experimental and model-calculated  $^{13}\text{C}$  NMR spectra of SG coking coal.



**Figure 6.** SG coking coal macromolecular structure model. (a) The 2D layout of the SG coking-coal macromolecule; (b) The 3D optimized structure of the SG coking-coal macromolecule.

The geometry-optimized 3D structure of the SG coking coal macromolecule (Figure 6b) reveals a pronounced tendency for the polyaromatic clusters to form face-to-face stacked arrangements, a key supramolecular feature not discernible from the 2D topology. To quantify this stacking, the interlayer distances between the centroids of parallel aromatic sheets were measured. The average interlayer spacing was found to be approximately  $3.48 \pm 0.15 \text{ \AA}$ , which falls within the typical range for van der Waals-dominated  $\pi$ - $\pi$  interactions in graphitic and turbostratic carbon materials and is slightly larger than the ideal graphite interlayer distance ( $3.35 \text{ \AA}$ ), reflecting the structural disorder introduced by heteroatoms and aliphatic bridges.

These stacked domains are stabilized primarily by  $\pi$ - $\pi$  interactions, which arise from the synergistic effect of van der Waals forces and weak electrostatic interactions between the  $\pi$ -electron clouds of adjacent aromatic systems. In our model, the naphthalene- and anthracene-dominated clusters exhibit the most significant overlap and thus contribute most strongly to this stabilizing interaction. The presence of heteroatoms (e.g., O in phenolic groups, N in pyridinic rings) modulates the local electron density, potentially creating dipole moments that can either enhance or slightly disrupt the ideal stacking, leading to the observed distribution of distances.

### 3.5. DFT Results Analysis

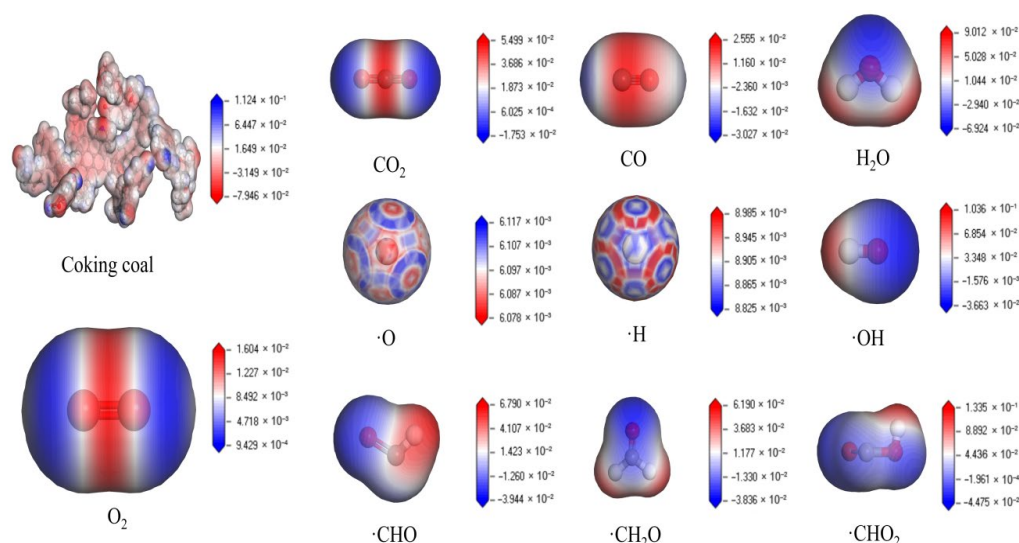
In the present study, we use ESP and FMO descriptors as semi-quantitative indicators of reactivity rather than performing full transition-state searches for all possible elementary steps. Nevertheless, the alignment between ESP–FMO hotspots and experimentally inferred oxidation-sensitive motifs (e.g., phenolic/etheric C–O, benzylic positions, heteroatom-substituted rings) provides a mechanistic bridge between the macromolecular structure of SG coal and its observed spontaneous-combustion tendency. Future work will extend this approach by calculating explicit energy barriers and rate constants for representative reactions at the key sites identified here.

#### 3.5.1. Electrostatic Analysis

The difference in the distribution of electrostatic potentials of the main gas molecules (e.g., CO<sub>2</sub>, CO, H<sub>2</sub>O, O<sub>2</sub>) and free radicals (e.g., ·O, ·H, ·OH, ·CHO, ·CH<sub>2</sub>O, ·CHO<sub>2</sub>) generated by the combustion of coking coal is shown in Figure 7 [42]. DFT-derived electrostatic potential (ESP) maps resolve where electron density accumulates (red, nucleophilic) or is depleted (blue, electrophilic), thereby rationalizing preferred collision partners in high-T oxidation. In Figure 7 the SG macromolecule shows a patchy surface: red lobes concentrate around O-containing groups (phenolic/ether/carboxyl), while blue belts appear on H-terminated edges and aliphatic bridges. These contrasts indicate that electron-deficient oxidants/radicals (e.g., ·OH, ·O) will be drawn to the red patches, whereas nucleophiles (if present) would target the blue domains. For stable gases, CO<sub>2</sub> exhibits a nearly centrosymmetric ESP with red at the O termini and a weakly blue carbon axis—consistent with low intrinsic polarity and chemical inertness; further oxidation requires high-energy activation. CO displays a pronounced dipole (C end blue, O end red), marking the carbon as the electrophilic site for attack by ·OH/·O to form the HOCO intermediate and ultimately CO<sub>2</sub>. H<sub>2</sub>O shows a strong red lobe at O and blue at H, explaining facile H-transfer and its role as both radical sink and source under dissociation. O<sub>2</sub> is almost ESP-uniform, indicating weak electrostatic steering; its participation relies on radical initiation rather than direct polar interactions. For radicals, ·OH presents the strongest charge separation (O red/H blue), consistent with its dual reactivity: H-abstraction from aliphatic C–H (attacking blue H sites) and addition to electron-poor carbon centers such as CO (blue C end). ·O features a highly negative ESP cap (red), underpinning its high nucleophilicity and propensity for addition/insertive oxidation at electrophilic carbons. ·H shows minimal anisotropy but extreme reactivity; its small, mildly blue potential favors fast H-abstraction and chain propagation. Polar carbonyl-bearing radicals—·CHO, ·CH<sub>2</sub>O, and ·CHO<sub>2</sub>—exhibit red density localized on O and blue on the formyl carbon; they therefore add O<sub>2</sub> or react with ·OH at the carbon center and decompose along pathways that funnel to CO/CO<sub>2</sub> while regenerating ·OH/·O.

The ESP map of the optimized SG macromolecule (Figure 7) reveals a pronounced heterogeneity of surface potential. The colour scale is set to cover the full range of computed ESP values on the van der Waals surface (from V<sub>min</sub> to V<sub>max</sub>, see Figure 7), so that red regions correspond to strongly negative potentials (electron-rich sites), whereas blue regions mark positive potentials (electron-deficient sites). Electron-rich “hotspots” are primarily located around phenolic and etheric C–O groups, carboxyl/carbonyl moieties, and in the vicinity of thiophenic sulfur, reflecting localized accumulation of  $\pi$ - and lone-pair density. In contrast, electron-poor “belts” appear along H-terminated aromatic edges and aliphatic bridges, where  $\sigma$ -bonding character dominates and the electron density is comparatively depleted. These ESP features imply that electrophilic and radical oxidants such as ·OH and ·HO<sub>2</sub> will preferentially attack the red hotspots (e.g., phenolic/etheric oxygen environments and activated benzylic positions), while nucleophilic species would

favour the blue belts if present. Molecular  $O_2$  and  $CO_2$ , being weakly polar and possessing relatively small permanent multipole moments, exert only limited steering based on ESP; their initial interactions with the coal surface are thus governed mainly by dispersion and local frontier-orbital overlaps rather than by strong electrostatic attraction.



**Figure 7.** Electrostatic potentials of SG coking coal molecules and major gases and radical products.

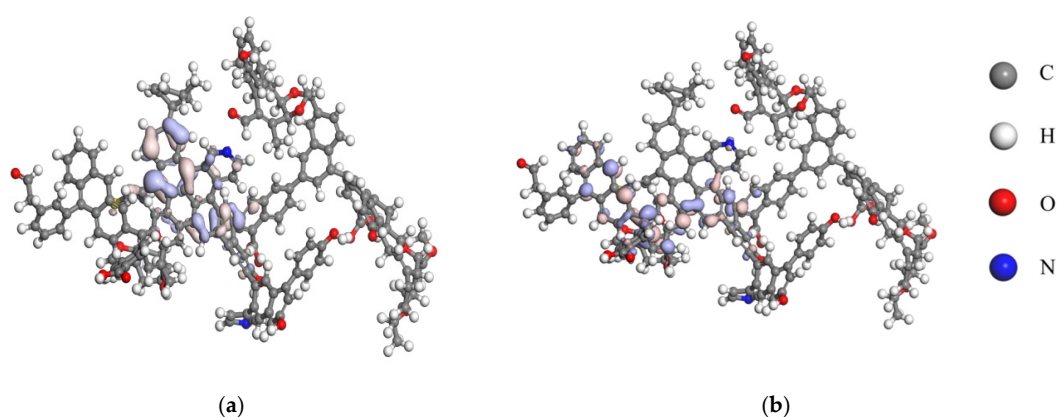
Taken together, the ESP patterns explain three features of coking-coal combustion chemistry: (i) symmetry-stabilized products ( $CO_2$ ,  $O_2$ ) show weak electrostatic driving forces; (ii)  $CO$  is predisposed to oxidation at the carbon end; and (iii) chain carriers ( $\cdot OH$ ,  $\cdot O$ ,  $\cdot H$ , formyl/peroxy radicals) possess strongly polarized potentials that steer selective H-abstraction and O-addition steps, sustaining the radical chain and accelerating conversion to  $CO_2/H_2O$ .

### 3.5.2. Frontline Molecular Orbital Analysis

According to the front orbital theory, the difference between the HOMO and LUMO energy levels can reflect the energy distribution of electrons in a molecule, which affects the activity and stability of the molecule in a chemical reaction. The LUMO and HOMO electron density distributions of SG coking coal are shown in Figure 8. As shown in Figure 8, the HOMO is predominantly a  $\pi$  orbital delocalized over the peri-condensed polyaromatic core (naphthalene/anthracene motifs) and partially extends onto the thiophenic ring; minor density appears on phenoxy oxygen lone pairs. These HOMO lobes co-localize with the red ESP patches identified previously, marking electron-rich, nucleophilic domains that are prone to attack by electrophilic oxidants ( $\cdot OH$ ,  $\cdot O$ ) via benzylic H-abstraction and aryl-edge addition. In contrast, the LUMO is concentrated on electron-withdrawing sites—carboxyl/carbonyl carbons, ether bridges, and ring carbons  $\alpha$  to pyridinic N—spatially overlapping the blue ESP belts. Such LUMO localization designates the preferred electron-accepting (electrophilic) centers, which are susceptible to nucleophilic oxygen insertion (e.g., by O-centered radicals after prior H-abstraction) and to charge-transfer steps along oxidation pathways.

Frontier-orbital analysis further refines this picture. As shown in Figure 8, the HOMO of the SG macromolecule is largely localized on fused aromatic rings and thiophenic moieties, especially along benzylic and edge carbons, whereas the LUMO is concentrated on carbonyl/ carboxyl groups, ether linkages, and aromatic carbons adjacent to pyridinic nitrogen. The corresponding HOMO and LUMO energy levels ( $E_{LUMO}$  and  $E_{HOMO}$ , with  $\Delta E = E_{LUMO} - E_{HOMO}$ , see Table 6) define a moderate HOMO–LUMO gap, consistent with

a material that is neither extremely inert nor overly reactive. Within conceptual DFT, such a gap translates into an intermediate chemical softness: SG coal is sufficiently “soft” to allow electron transfer and radical addition at specific sites, but retains enough overall stability to maintain its aromatic framework under moderate thermal loads. The spatial separation of HOMO- and LUMO-dominated regions means that electron donation (oxidation) is most facile at the HOMO-rich aromatic/thiophenic domains, whereas electron acceptance and subsequent bond formation are favoured at LUMO-rich carbonyl/ether and N-adjacent sites. This orbital complementarity underlies the site-selective oxidation pathways inferred for SG coal, in which “benzylic H-abstraction and edge addition  $\rightarrow$  oxygen insertion/charge transfer  $\rightarrow$  formation of  $\text{CO}_2/\text{H}_2\text{O}$ ” occurs preferentially at structurally and electronically activated edge segments.



**Figure 8.** HOMO and LUMO electron density distribution of SG coking coal. (a) HOMO. (b) LUMO.

The joint ESP–FMO map therefore predicts a site-selective reactivity hierarchy: (i) HOMO-rich aryl edges and thiophene  $\alpha$ -positions  $\rightarrow$  facile electrophilic attack by  $\cdot\text{OH}/\cdot\text{O}$ , initiating chain reactions; (ii) LUMO-rich carbonyl/carboxyl carbons and N-activated ring carbons  $\rightarrow$  favored oxygen addition and ring-opening/fragmentation during deep oxidation; (iii) sparsely substituted alkyl side chains exhibit lower orbital density and thus lower intrinsic reactivity, consistent with the moderate disorder inferred from Raman and the limited oxygenated groups from XPS. Although the absolute HOMO–LUMO gap governs global reactivity, the spatial separation of HOMO (donor) and LUMO (acceptor) is the key determinant for where oxidation is triggered and propagated across the SG macromolecule.

#### 4. Conclusions

This study established and optimised a compositionally realistic macromolecular model of Shigang (SG) coking coal and employed density functional theory (DFT) based electrostatic potential (ESP) and frontier molecular orbital (FMO) analysis to interrogate its combustion-related reactivity at the molecular and electronic levels. By jointly constraining the model with proximate/ultimate analyses, XPS, solid-state  $^{13}\text{C}$  NMR and Raman spectroscopy, and by validating it against the experimental  $^{13}\text{C}$  NMR envelope, we obtained a naphthalene-dominant macromolecular architecture ( $\text{C}_{190}\text{H}_{144}\text{N}_{20}\text{O}_{21}\text{S}$ ) that faithfully reproduces the rank, heteroatom speciation and aromatic condensation of SG coking coal. On this basis, ESP–FMO mapping was used to identify electron-rich “hotspots” and electron-poor “belts” that control site-selective oxidation along combustion-relevant pathways. The main conclusions are as follows:

- (1) Integrated XPS,  $^{13}\text{C}$  NMR and Raman constraints yield a macromolecular model in which aromatic/aliphatic C–C/C–H dominates the carbon skeleton, oxygen is mainly present as phenolic/etheric C–O with minor carbonyl/carboxyl C=O, nitrogen occurs

primarily as pyrrolic and pyridinic N, and sulfur is partitioned between thiophenic and oxidised forms. The aromatic fraction ( $f_a' \approx 68\%$ ) and bridgehead-to-periphery ratio ( $X_{BP} = 0.215$ ) indicate moderately condensed, naphthalene-dominant fused-ring domains with relatively few alkyl side chains but a substantial population of accessible edge carbons. The model composition  $C_{190}H_{144}N_2O_{21}S$  reproduces the experimental ultimate analysis within  $\pm 0.5$  wt% for all elements, and the model-predicted  $^{13}C$  NMR envelope is in good agreement with the measured spectrum, confirming that the structural and compositional features of SG coal are captured consistently.

- (2) ESP–FMO mapping elucidates oxidation hotspots and site-selective reactivity. ESP maps reveal pronounced electron-rich regions around phenolic/etheric C–O groups, carboxyl/carbonyl moieties and thiophenic environments, contrasted by electron-poor belts along H-terminated aromatic edges and aliphatic bridges. FMO analysis shows HOMO density concentrated on fused aromatics and thiophenic units, whereas LUMO density is localised on carbonyl/ether groups and aromatic carbons adjacent to pyridinic N, with a moderate HOMO–LUMO gap indicative of intermediate chemical softness. This spatial separation of HOMO- and LUMO-dominated regions provides an electronic basis for site-selective oxidation: benzylic and edge carbons in HOMO-rich domains are predisposed to H-abstraction and radical initiation, while LUMO-rich oxygenated and N-adjacent sites favour subsequent oxygen addition and charge transfer, ultimately promoting  $CO_2/H_2O$  formation at specific structural motifs rather than uniformly over the macromolecular surface.
- (3) Practical implications for controlling coal oxidation and spontaneous combustion. The identified reactive motifs—phenolic/etheric C–O sites, benzylic/edge carbons and heteroatom-substituted aromatic units—are precisely those that dominate the ESP–FMO hotspots and thus represent key levers for industrial control. In practical terms, these insights can inform (i) targeted strategies for managing low-temperature oxidation (e.g., inertisation and ventilation schemes that focus on zones enriched in highly reactive, defect-rich coal), (ii) rational design or selection of chemical inhibitors and additives that preferentially adsorb on, cap or scavenge radicals at phenolic/etheric and benzylic sites, and (iii) more mechanistically grounded risk assessment tools that link coal quality, structural parameters ( $f_a$ ,  $X_{BP}$ ,  $I_D/I_G$ ) and storage conditions to spontaneous-combustion propensity. The macromolecular model and ESP–FMO descriptors thus provide a transferable framework for bridging laboratory characterisation with field-scale safety management.
- (4) Limitations and future perspectives. The present work is subject to several limitations. First, the SG model represents a single, “average” macromolecular structure derived from bulk characterisation data; it cannot capture the full structural heterogeneity of real coal particles or the potential catalytic influence of mineral inclusions. Second, the DFT calculations are performed on isolated molecules and fragments in the gas phase, without explicit treatment of condensed-phase packing, transport processes or full kinetic pathways. As a result, the ESP–FMO descriptors used here provide semi-quantitative indicators of relative reactivity rather than explicit rate constants or ignition thresholds. Future work will address these limitations by (i) performing ReaxFF-based molecular dynamics simulations on the SG macromolecular model to follow dynamic oxidation pathways and radical evolution under controlled temperature and atmosphere; (ii) extending the multi-probe-constrained modelling and ESP–FMO analysis to coals of different rank and geological origin to establish more general structure–reactivity correlations; and (iii) applying the same electronic-structure framework to adsorption and catalytic phenomena, including the interaction of inhibitors, inerting gases ( $O_2/CO_2/N_2$ ) and

mineral phases with coal macromolecular “hotspots”. Such efforts will further refine the mechanistic understanding of coal oxidation and spontaneous combustion and support the development of more effective, structure-guided mitigation strategies.

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