ABSTRACT: The structural characteristics of coal at the molecular level are important for its efficient use. Bituminous coal from the Baozigou Coal Mine is investigated, using elemental analysis, $^{13}$C nuclear magnetic resonance, X-ray photoelectron spectroscopy, and Fourier transform infrared. The molecular structure was determined. The aromatic compounds of bituminous coal molecules are primarily two- and three-ring structures, and the aliphatic structures are primarily in the form of methyl, ethyl side chains, and napthenic hydrocarbons. The ratio of aromatic bridge carbon to peripheral carbon in the molecular structure is 0.279. Oxygen atoms in the form of carbonyl, phenolic hydroxyl and C−O, and nitrogen atoms in pyrroles. Thus, the average structure model of bituminous coal macromolecules was constructed; the molecular formula was C$_{169}$H$_{128}$O$_{10}$N$_2$S, and the molecular weight was 2378. The aromatic structural units in the macromolecular structure of coal include four naphthalenes, three anthracenes, two tetracenes, and heteroatoms in the form of three carbonyl groups, one phenolic hydroxyl group, one pyrrole, and one pyridine. The structure optimization and annealing kinetic simulation of a single macromolecular structure model were performed. Chemical bonds such as bridge bonds and aliphatic bonds were found to be twisted, and π−π interactions between the aromatic sheets in the molecule produced adjacent aromatic sheets. This arrangement tends to be approximately parallel, and the total energy decreases from 6713.401 to 2667.595 kJ/mol, among which the bond stretching energy and van der Waals energy dominate. We used 20 bituminous coal macromolecular models to construct aggregated structural models. After optimization by molecular dynamics simulation, the macromolecules were constrained by the surrounding molecules, and the sheet-like aromatic carbon structures that were originally approximately parallel were distorted. The macromolecular structure model of bituminous coal constructed in this study provides a theoretical model basis for the optimal surfactant.

1. INTRODUCTION

With the improvement of coal mine production systems, coal dust pollution remains one of the five major factors contributing to coal mine disasters. Particularly, in various mining working faces, the production of coal dust in the efficient production process of coal mines can seriously endanger the health of miners, and the accumulation and diffusion of coal dust concentrations seriously endanger normal production underground work. Pneumoconiosis can occur after exposure to a high-concentration coal dust operation environment over the long term. Supressing dust production at its source has always been a difficult problem. However, the physical properties of coal dust are hydrophobic, and increasing the contact between the solution and coal dust is an important factor in inhibiting its release and diffusion. Accelerating the contact efficiency of the solution and coal dust can effectively improve the underground working and production environment. To effectively improve the production environment of each mining face, we investigate the bituminous coal from the Baozigou Coal Mine, Shanxi Province, and use various spectral analyses to determine coal structure parameters, establish its structure, and the properties of bituminous coal at the molecular level.

Ping et al. used a combination of X-ray photoelectron spectroscopy (XPS), $^{13}$C nuclear magnetic resonance (NMR), and Fourier transform infrared (FT-IR) to establish three-dimensional (3D) molecular models of vitrinite and inertite, whose molecular formulas are C$_{126}$H$_{99}$O$_{12}$N$_3$S$_2$ and C$_{131}$H$_{98}$O$_{179}$S$_2$, respectively, the predicted spectra demonstrate that these models are able to reflect the true molecular structure of coal. Lin et al. established structural models of raw coal, ldi and hdi from $^{13}$C NMR, FT-IR, and XPS. The characterization data and
molecular structure model showed no significant difference in the aromaticity. The structural units of all the samples were nearly identical. Wang et al. used $^{13}$C NMR and FT-IR to construct small molecular structures of different coal samples and analyzed the evolution process of different coal qualities. He et al. analyzed the chemical structures of metamorphic coals with different grades from lignite to anthracite using FT-IR and $^{13}$C NMR, and concluded that the evolution structure of coal is complex and has three stages, with $R_o = 0.4–1.3, 1.3–2.0,$ and $2.0–4.0$%, respectively. When $R_o = 0.4–1.3$%, the rapid decline of oxygen-containing functional groups accompanied by enrichment is the main feature of aliphatic compounds. Currently, scholars have proposed more than 130 average structure models of coal molecules through research on the coal structure, and the most commonly used structural models are Fuchs, Given, Wiser, and Shinn. These models can explain the swelling, cracking, gas adsorption, and flotation behavior of coal to some extent. Using FT-IR and image processing techniques on coal structures, the image distribution is analyzed to determine the size and distribution of aromatic fused rings and combined with other testing and analysis techniques to construct ideal coal molecular structural models.

Bituminous coal from the Baozigou Coal Mine is investigated in this study using industrial analysis, elemental analysis, $^{13}$C NMR, FT-IR, and XPS. The molecular structure was studied by various means, and the average molecular structure model was constructed accordingly. The structure was optimized by the kinetic optimization algorithm in the Forcite module of Materials Studio software, and the optimization model was simulated by annealing dynamics. To use a molecular dynamics simulation to study the evolution of the crystallite structure of the coal at the molecular scale, the evolution of the crystallite structure provides a basis for the model and the pore volume of the Baozigou bituminous coal is given.

2. EXPERIMENTAL MATERIALS AND METHODOLOGY

2.1. Experimental Coal Samples. Experimental coal samples were selected from bituminous coal from the 10,103 mining face of the Baozigou Coal Industry Company (the density of coal is 1.3 g/cm$^3$). The national standard GB/T 482–2008 was selected from the #9 coal seam for sampling. Coal samples with marked defects were eliminated, and intact coal samples were ground into 200 minus in the laboratory. The samples were placed in a constant-temperature oven at 80 °C for continuous drying for 24 h, and then the coal samples were subjected to coal analysis, NMR experiments, XPS experiments, and FT-IR.

2.2. Elemental Composition. To construct the molecular structure model of the Baozigou Coal Mine, the elemental industrial analysis of Baozigou coal samples was performed using a German Allimonta unicyclic element analyzer, and the elemental contents of C, H, N, and S were determined. The O content was calculated by the subtraction method, and the results of industrial element analysis are shown in Table 1.

2.3. FT-IR Experiment. FT-IR was performed using the KBr pellet method. The raw ore sample and KBr powder were weighed and mixed at a ratio of 1:200, fully ground in anagate mortar, pressed into a transparent sheet with a thickness of approximately 0.5 mm, and dried in an oven at 110 °C for 6 h. The FT-IR test was completed using a Nicolet6700 FT-IR spectrometer that was produced by Thermo Fisher Company in the United States, with a resolution of 4 cm$^{-1}$, accumulative scanning times of 32 times, and a measured spectral range of 400–4000 cm$^{-1}$.

Spectral analysis can be performed to determine which compounds or functional groups exist in the sample. With a clear absorption peak position, the content of these compounds or functional groups can also be quantitatively analyzed. The absorption peaks in the IR spectrum of coal can be divided into four types: (1) aromatic structures with absorption peaks at 900–700 cm$^{-1}$; (2) $\equiv$C stretching vibration and $-\text{CH}_3, -\text{CH}_2$ deformation vibration, and other structures; (3) the absorption peak is located in the fat structure of 3000–2800 cm$^{-1}$; and (4) the absorption peak is located in the hydroxyl structure of 3000–3600 cm$^{-1}$.

2.4. $^{13}$C NMR Experiment. The solid-state C spectrum analysis used a Bruker AVANCE III HD 400 MHz solid-state NMR spectrometer and a H/X dual-resonance solid-state probe with a 4 mm ZrO$_2$ rotor as the benchmark. The rotational speed was 5 kHz, and the detection resonance frequency of $^{13}$C was 100.625 MHz. The sampling time was 5.12 ms, the spectral width was 50 kHz, and the loop delay time was 6.5 μs.

2.5. XPS Experiment. The coal samples were tested using an X-ray photoelectron spectrometer (Thermo Fisher, ESCA-LAB Xi+, USA). The pressure of the analysis chamber reached 8 ×10$^{-10}$ Pa, the excitation source was Al kα radiation ($h \nu = 1486.6$ eV), the working voltage was 12.5 kV, the filament current was 16 mA, and the signal accumulation occurred over 10 cycles. The full passing energy spectrum was 100 eV, the narrow spectrum was 30 eV, the step size of each step was 0.05 eV, the residence time of the test was 40–50 ms, and charge correction was performed with a binding energy of C1 s = 284.80 eV as the energy standard. Finally, the C1 s, O1 s, N1 s, and S2 p nuclear magnetic spectra of the carbon spectrum were tested in the form of data.

2.6. Low Temperature Nitrogen Adsorption Experiment. The nitrogen adsorption experiment was completed using the JW-ZQ200 cryogenic liquid nitrogen adsorption instrument. The samples were ground, crushed, and screened to 200 minus. 2 g of samples were taken, dried in a drying box at a constant temperature of 60 °C for 24 h, and vacuum degassed for 24 h. During the adsorption experiment, the saturation pressure was maintained at 77.35 K, liquid nitrogen with a purity of more than 99.999% was used as the adsorbate, and the adsorption experiment was carried out at a relative pressure of 0.01–0.999.

2.7. Molecular Dynamics Simulation Method. To determine the lowest energy configuration of the single-molecule structure model, geometry optimization and annealing kinetic simulation of the single-molecule structure model of bituminous coal were performed using Materials Studio software. The molecular structure of bituminous coal was imported into Materials Studio software, and its structure was saturated and hydrogenated. The geometric optimization of the simulation adopts the Forcite module, and the Smart Minimizer method was used for optimization. The parameters are set as follows: the Coulomb energy and van der Waals energy were...
calculated based on the total energy of the atom. The net charge of the atom was obtained by the charge balance method, the number of iteration steps was 5000 steps, and the convergence criterion was fine. After geometry optimization, high-temperature relaxation was continued with the anneal of the Forcite module. The simulation process was performed under the NVT ensemble, and the Nosé temperature control method was selected. The initial temperature was set to 298 K, and the maximum temperature was set to 898 K. The heating rate was 50 K/time, and the simulation time was 200 ps.

Using the amorphous cell module in Materials Studio software, 20 optimized bituminous coal molecules were randomly added into a unit cell with a size of $36.4 \times 36.4 \times 36.4$ Å$^3$, and 3D periodic boundary conditions were added. The density of the structural model was set to 1.3 g/cm$^3$, and the system was first relaxed by a geometric optimization molecular dynamics simulation, followed by an annealing kinetic simulation with the temperature set at 298$\sim$898 K and the final temperature kept at 298 K. The configuration system with the lowest energy was selected as the structure model of bituminous coal molecular aggregates under periodic boundary conditions.

### 3. RESULTS AND DISCUSSION

3.1. FT-IR Analysis. 3.1.1. Hydroxyl Absorption Peak.

Hydroxyl groups in coal primarily exist in the end groups and side chains, which are important factors for the formation of hydrogen bonds in coal, generally determining the reaction properties of coal. Hydroxyls have a strong activation effect when breaking and cross-linking bonds. There are eight characteristic peaks in the FT-IR fitting spectrum of hydroxyl groups in Baozigou coal, as shown in Figure 1 ($R^2 = 0.996$). The specific absorption location data results are shown in Table 2.

According to Table 2, there is a hydroxyl absorption peak near the 3450 cm$^{-1}$ absorption peak position. The hydroxyl groups in coal are generally hydrogen bonded, and the spectral peak position shifts from 3300 cm$^{-1}$, where the general hydroxyl group appears, to 3450 cm$^{-1}$. With increasing the coalification degree, the absorption peak gradually weakened, indicating that the number of hydroxyl groups decreased. At 3030 cm$^{-1}$, it is the absorption peak of aromatic hydrogen, and the intensity of the peak reflects the degree of polycondensation of the aromatic nucleus of the coal structure. The hydrogen bond with the hydroxyl group formed on the aromatic ring is the most important hydroxyl structure of bituminous coal, accounting for 64.89%.

This result indicates that the cyclization of the aliphatic chain in coal has a strong condensation effect with functional groups, which weakens the stretching vibration of free hydroxyl groups.

3.1.2. Aliphatic Hydrocarbon Structure. The aliphatic hydrocarbon structures in coal include chain aliphatic hydrocarbons and cyclic aliphatic hydrocarbons. There are five fitting characteristic peaks in the aliphatic hydrocarbon structure in Figure 2. The original peak map, Peak fitting, and Cumulative peak fitting are shown.

| spectral position | peak type | peak weighted center (cm$^{-1}$) | fwhm | peak area | peak area percentage (%) |
|-------------------|-----------|---------------------------------|------|-----------|--------------------------|
| aromatic hydrogen | Gaussian  | 3004.82                         | 31.30| 0.73      | 3.14                     |
| aromatic hydrogen | Gaussian  | 3040.19                         | 64.62| 6.59      | 28.18                    |
| aromatic hydrogen | Gaussian  | 3176.76                         | 202.25| 3.64      | 15.56                    |
| aromatic hydrogen | Gaussian  | 3299.71                         | 160.72| 4.22      | 18.01                    |
| aromatic hydrogen | Gaussian  | 3388.61                         | 116.86| 4.19      | 17.89                    |
| hydrogen bonded   | Gaussian  | 3454.54                         | 85.19 | 3.06      | 13.05                    |
| −OH               | Gaussian  | 3521.01                         | 44.28 | 0.79      | 3.41                     |
| hydrogen bonded   | Gaussian  | 3556.28                         | 20.01 | 0.18      | 0.76                     |

Table 2. FT-IR Analysis Table of Hydroxyl Groups in Coal.
methine accounted for 16.71%. The proportion of methylene groups in the aliphatic hydrocarbon structure is 41.89%. Methylene accounted for 41.40%, and the proportion of methyl groups is 29.16%. Vibrations of methyl groups, methylene groups, and methine groups generally have peaks of 1300 cm$^{-1}$ and 2800 cm$^{-1}$.

3.2. XPS Photoelectric Spectroscopy Analysis. The XPS energy spectrum test results of the bituminous coal samples are shown in Figure 5a. Different peak positions in the spectrum correspond to different element forms.

3.3. 13C NMR Carbon Spectrum Analysis. As shown in Figure 5b, the C spectrum is divided into four peak positions after fitting. The peak at 284.70 eV can be attributed to C–C and C–H, and the C structure accounts for 69.08%; the peak at 285.54 eV can be attributed to C–O in ether and hydroxyl groups, accounting for 21.09% in the C structure; the peak at 286.64 eV can be attributed to C=O in the carbonyl group, accounting for 4.62% in the C structure; and the peak at 289.46 eV can be attributed to COO$-$ in the carboxyl group, which accounts for 5.21% of the C structure.

The O spectrum is shown in Figure 5c. After peak fitting, a total of three peak positions are divided. The peak at 530.9 eV can be attributed to carbonyl oxygen C=O, which accounts for 32.49% of the O structure; the peak at 532.11 eV can be attributed to the carbon–oxygen single bond C–O, accounting for 22.54% of the O structure; and the peak at 533.54 eV can be attributed to the carboxyl oxygen COO$-$, accounting for 43.20% of the O structure.

The N spectrum is shown in Figure 5d. A total of three peak positions are obtained after peak split fitting: the peak at 397.23 eV can be attributed to pyridine, and the proportion of the N structure is 15.88%; the peak at 400.21 eV can be attributed to pyrrole, which accounts for 25.29% of the N structure; and the peak at 401.62 eV can be attributed to quaternary nitrogen, which accounts for 58.83% of the N structure.

The S spectrum is shown in Figure 5e. A total of three peak positions are divided. The peak at 284.70 eV can be attributed to thiophenes, accounting for 32.49% of the S structure; the peak at 285.54 eV can be attributed to low-valent organic sulfides, which accounts for 40.55% of the S structure; and the peak at 289.46 eV can be attributed to inorganic sulfate, accounting for 25.29% of the S structure.

3.3. 13C NMR Carbon Spectrum Analysis. The chemical shift of 13C NMR is sensitive to the chemical environment and directed relative content. The proportion of phenolic C–O and ether bonds in bituminous coal is 53.88%, the proportion of –CH$_3$ is 7.58%, and the proportion of carbonyl groups is 2.34%. These results show that the oxygen-containing functional groups of bituminous coal primarily exist in C=O bonds and aromatic rings.

3.1.4. Aromatic Hydrocarbon Structure. There are six characteristic peaks in the bituminous coal aromatic hydrocarbon structure (Table 5). The fitting spectrum is shown in Figure 2, and the peak structure attribution and relative content are shown in the table. According to Table 6, the aromatic hydrocarbon structure in bituminous coal primarily. The content of disubstituted benzene (2H) rings in bituminous coal was 37.95%, that of monosubstituted benzene (1H) rings was 29.16%, and that of tetra-substituted benzene (4H) rings was 32.89%. Disubstituted and trisubstituted substitutions in bituminous coal are the primary structures of coal molecules (Figure 4).

Table 4. FT-IR Analysis Table of Oxygen-Containing Functional Groups in Coal

| spectral position attribution | peak type | peak weighted center (cm$^{-1}$) | fwhm | peak area | peak area percentage (%) |
|-----------------------------|-----------|-------------------------------|------|-----------|--------------------------|
| Si–O                        | Gaussian  | 1018.86                       | 66.45| 16.81     | 11.78                    |
| C–O                         | Gaussian  | 1079.56                       | 73.48| 8.49      | 5.96                     |
| C–O                         | Gaussian  | 1109.57                       | 135.09| 14.12     | 9.91                     |
| C–O                         | Gaussian  | 1180.77                       | 99.21| 10.91     | 7.64                     |
| C–O                         | Gaussian  | 1268.94                       | 122.32| 20.36     | 14.28                    |
| CH$_2$–Ar, R                | Gaussian  | 1387.78                       | 140.16| 32.58     | 22.84                    |
| CH$_3$                      | Gaussian  | 1443.93                       | 43.23| 7.58      | 5.31                     |
| C=O–C                      | Gaussian  | 1508.48                       | 107.83| 9.01      | 6.32                     |
| C=O–C                      | Gaussian  | 1598.83                       | 67.75| 19.72     | 13.83                    |
| C=O–C                      | Gaussian  | 1660.64                       | 30.11| 2.34      | 1.64                     |
| carbonyl acids              | Gaussian  | 1731.69                       | 25.14| 0.69      | 0.49                     |

The XPS fitting diagram of coal oxygen-containing functional groups.

Table 5. FT-IR Analysis Table of the Aromatic Hydrocarbon Structure in Coal

| spectral position attribution | peak type | peak weighted center (cm$^{-1}$) | fwhm | peak area | peak area percentage (%) |
|-----------------------------|-----------|-------------------------------|------|-----------|--------------------------|
| 4H                          | Gaussian  | 743.65                        | 20.61| 1.21      | 12.26                    |
| 4H                          | Gaussian  | 753.99                        | 25.29| 2.04      | 20.63                    |
| 2H                          | Gaussian  | 803.54                        | 38.42| 3.75      | 37.95                    |
| 1H                          | Gaussian  | 855.74                        | 33.89| 1.11      | 11.25                    |
| 1H                          | Gaussian  | 871.62                        | 26.29| 1.77      | 17.91                    |

Figure 3 shows that the 13C NMR spectrum can be roughly divided into five peaks based on chemical shifts: (1) aliphatic
carbon peaks with chemical shifts of 0–60 ppm; (2) ether oxygen peaks with chemical shifts of 60–90 ppm; (3) chemical shifts of 100–165 ppm for the aromatic carbon peak; (4) the carboxyl carbon peak with a chemical shift of 165–188 ppm; and (5) the carbonyl carbon peak with a chemical shift of approximately 188–220 ppm. The figure shows that two relatively high spectral peaks appear in the bituminous coal sample, and the chemical shifts in the range of 0–60 ppm are aliphatic and methine carbon structures. The chemical shifts are in the 100–165 ppm range for the structures of protonated aromatic carbons, bridgeheads, and side-branched aromatic carbons. The peak intensity at 100–165 ppm is much higher than that at 0–60 ppm. This result indicates that the aromatic organic molecular structure in the bituminous coal samples is the primary component, while the aliphatic methyl carbon and methine carbon are the secondary components. To facilitate the division of chemical structures at different shifts, the assigned structures of carbon chemical shifts of 13C NMR are shown in Table 6.

**Table 6. Structure Assignment of Chemical Shifts in 13C NMR Spectra**

| Carbon structure name | Primary attribution | Typical chemical shift/10^6 | Carbon structure name | Primary attribution | Typical chemical shift/10^6 |
|-----------------------|---------------------|-----------------------------|-----------------------|---------------------|-----------------------------|
| Lipid methyl carbon   |                     | 14-16                       | Protonated aromatic carbon |                     | 100-129                    |
| Aromatic methyl carbon|                     | 16-22                       | Bridgehead aromatic carbon |                     | 129-137                    |
| Mesomethylene carbon  |                     | 22-36                       | Side branch aromatic carbon |                     | 137-148                    |
| Methylene carbon      |                     | 36-50                       | Oxygen substituted aromatic carbon |                     | 148-165                    |
| Oxyymethylene carbon  |                     | 60-70                       | Carbonyl carbon       |                     | 165-188                    |
| Oxygen-grafted carbon |                     | 75-90                       | Carbonyl carbons of aldehydes, quinones, phenyl ketones Carbonyl carbon of alkane and cycloalkane |                     | 205-220                    |

**Figure 4.** FT-IR fitting spectrum of the aromatic hydrocarbon structure in coal.
NMR to determine the content and position of each functional group. Peakfit software was used to perform the peak fitting operation on the $^{13}$C NMR data. Peak positions were added as completely as possible to ensure a higher degree of fit and accuracy, and the peak processing results agreed more with the experimental results. The carbon structure was assigned numerically (Table 2), and the proportion of the carbon skeleton structure and structural parameters were calculated by the relative area of the subpeaks.

The $^{13}$C NMR test results of the carbon NMR spectrum of the bituminous coal sample show that the primary chemical shifts of the sample appear at $(0-70) \times 10^{-6}$, $(100-170) \times 10^{-6}$, and $(210-250) \times 10^{-6}$ places. After the peak split fitting operation, a total of 32 peak positions were added, and the fitting results fit the original spectrum, as shown in Figure 2. After calculating the relative area of each peak position and summarizing it, the proportion of protonated aromatic carbon in the coal sample is shown to be the highest, followed by bridgehead aromatic carbon, methylene carbon, and methine carbon. The carbonyl groups of aldehydes, quinones, and phenyl ketones account for 0.082%, which is negligible (Tables 7 and 8).

3.3.2. $^{13}$C NMR Structure Analysis. To study the relative content of carbon atoms with different functional groups, Solum et al. proposed 12 structural parameters of coal based on previous studies, including $\delta^C$ (a total aromatic carbon rate), $\delta^C_{C}$ (a...
Table 7. Structure Attribution and Relative Area

| structural attribution                        | structural proportions % |
|----------------------------------------------|--------------------------|
| protonated aromatic carbon                   | 22.161                   |
| bridgehead aromatic carbon                   | 19.698                   |
| methylene carbon and methine carbon         | 19.255                   |
| methine carbon and quaternary carbon        | 11.987                   |
| side branch aromatic carbon                 | 10.166                   |
| oxygen-substituted aromatic carbon          | 7.151                    |
| oxygen to methyl and oxygen to methylene carbon | 4.697               |
| aromatic methyl carbon                      | 1.455                    |
| carbonyl carbon of alkanone and cycloalkanone | 1.446               |
| oxygen to methine carbon                    | 1.130                    |
| aliphatic methyl carbon                     | 0.771                    |
| carbonyl carbons of aldehydes, quinones, and phenyl ketones | 0.082                |

The 12 structural parameter values of bituminous coal samples were obtained by calculating the data, and the $X_{BP}$ value of the aromatic bridge carbon to weekly carbon ratio calculated by Formula 1 was 0.279. In the benzene ring structure, the $X_{BP}$ value of benzene was 0, the $X_{BP}$ value of naphthalene was 0.25, the $X_{BP}$ value of anthracene was 0.4, the $X_{BP}$ value of tetracene was 0.5, and the $X_{BP}$ value of pentacene was 0.57. To control the molecular weight and reduce the computational complexity of the simulation, the structure ratio in the aromatic structure was adjusted and combined with the XPS data analysis results. The combination of four naphthalene, three anthracene, and two tetracene was finally determined. Aliphatic carbon structures exist in the form of methylene, methine, aliphatic side chains, and cycloalkanes. According to the analysis results of the carbon structure attribution in the table, the aliphatic carbons in this model were primarily methylene and methine carbons, while the proportion of aliphatic methyl carbons was nearly zero. The alkyl side chains were dominated by long-chain and naphthenic hydrocarbons.

According to the analysis of the abovementioned experimental results, the total number of carbon atoms in the structural model was 150—170. According to the element content of the element industry analysis, the molecular structure plane unit model of bituminous coal was constructed. The plane unit model of the molecular structure of bituminous coal was drawn using kngdraw software and the molecular structure was C$_{169}$H$_{128}$O$_{10}$N$_{2}$S, as shown in Figure 8.

![Figure 8. Planar model of the molecular structure of Baogou coal.](https://doi.org/10.1021/acsomega.2c00505)
bridge carbon and the position of heteroatoms in the structure of different coal samples were determined. Combined with the elemental analysis of C, H, O, N, and S, the content of coal was preliminarily constructed. However, the constructed planar model may be different from the correct model due to the position of functional groups, and the initial model is continuously adjusted and optimized. This step was performed using 13C spectral prediction in MestRenova software. The comparison between the final adjusted model and the original data model is shown in Figure 9.

### 3.5. Molecular Structure and Model Construction of Bituminous Coal Samples

The structure with the lowest energy in the simulation results was selected as the optimal geometry of the bituminous coal, as shown in Figure 10. After the optimization of molecular mechanics and molecular dynamics, some chemical bonds, such as bridge bonds and aliphatic bonds, were twisted to achieve the minimum repulsion between functional groups in the single molecular structure. Because of the $\pi-\pi$ interaction between the aromatic rings, the adjacent aromatic sheets tended to be arranged in parallel, and the interlayer spacing increased, exhibiting a 3D effect. Table 9 shows the energy composition of the bituminous coal structure model before and after optimization. The total energy was 6713.401 kJ/mol before optimization and 2667.595 kJ/mol after optimization, indicating a marked reduction in total energy. In the optimized model, the bond stretching energy and van der Waals energy decreased, other terms increased, and the total energy markedly decreased, indicating that the bond stretching energy and van der Waals energy were dominant in the structure, and the bond stretching energy belonged to valence electrons. The van der Waals energy is a nonbonding energy. Because coal is a macromolecular structure composed of multiple aromatic rings, the molecular model of bituminous coal was transformed in the simulation from a two-dimensional planar structure into a 3D structure. The energy and torsional energy increased and concurrently caused a reduction in the bond stretching potential energy. In the optimized 3D structure, the parallel arrangement of aromatic sheets produced a larger dispersion force, which was the primary reason for the observed decrease in van der Waals energy (Table 10).

### 3.6. Establishment of the Molecular Aggregation Structure Model of Bituminous Coal

The aggregated structure model shows that the molecular structure is bent and twisted after optimization by molecular mechanics and molecular dynamics simulation. Because coal is an amorphous substance without long-range periodicity and restricted by surrounding molecules, the original approximated flat fragrant carbon structure is twisted and deformed. Figure 11 shows that the molecular distribution of Baozigou coal is relatively uniform, and the oxygen-containing functional groups on the surface are uniformly distributed. The occupied volume of the coal was 42025.14 Å³, the pore volume was 6534.86 Å³ (1.66 cc/g), and the surface area was 9985.43 Å², thus describing the structural characteristics of the Baozigou coal sample surface (Figure 12).

### 3.7. Analysis of Liquid Nitrogen Adsorption Experiment

The nitrogen adsorption and analytical curves of the coal samples are shown in Figure 11. When the relative pressure is 0.01—0.2, the adsorption capacity rises steadily, when the relative pressure is 0.2—0.8, the adsorption capacity rises relatively gently, and when the relative pressure is 0.8—0.995, the adsorption capacity increases more obviously. When the relative pressure was 0.995, the maximum adsorption amount was 1.68 cc/g. The difference from the constructed model is 0.02 cc/g, which proves the accuracy of the model establishment.

### Table 9. Energy Composition of the Bituminous Coal Structure Model

| state   | total energy | bond     | angle   | torsion | inversion | van der Waals | electrostatic |
|---------|--------------|----------|---------|---------|-----------|---------------|---------------|
| initial | 6713.401     | 1225.408 | 308.759 | 3106.939| 131.147   | 1343.187      | −93.181       |
| finally | 2667.595     | 56.135   | 112.354 | 2643.820| 48.999    | 103.501       | −173.839      |

### Table 10. Pore Volume Parameters of Bituminous Coal Molecular Aggregates

| occupied volume (Å³) | free volume (Å³) | surface area (Å²) |
|----------------------|------------------|------------------|
| 42025.14             | 6534.86          | 9985.43          |
4. CONCLUSIONS

(1) According to $^{13}$C NMR, 12 structural parameters of the Baozigou bituminous coal structure were obtained, and the ratio of aromatic bridge carbon to peripheral carbon in the molecular structure of the coal was calculated to be 0.279. The combined test results of $^{13}$C NMR, XPS, and FT-IR showed that bituminous coal’s carbon atoms in the coal sample are primarily aromatic carbon structures. The aromatic structural units in the coal sample include four naphthalene, three anthracenes, and two tetracene. The heteroatoms in the coal molecular structure are three carbonyls, where one exists as phenolic hydroxyl, one pyrrole, and one pyridine. The final constructed bituminous coal had a molecular formula of $C_{169}H_{128}O_{10}N_{2}S$ and a molecular weight of 2378.

(2) After geometric optimization and molecular dynamics simulation of a single molecular structure model using Materials Studio software, chemical bonds such as bridge bonds and aliphatic bonds were found to be twisted, and the $\pi-\pi$ interaction between the aromatic sheets in the molecule made the adjacent aromatic sheets. The lamellae tended to be approximately parallel to each other. The total molecular energy before and after optimization decreased from 6713.401 to 2667.595 kJ/mol, and bond stretching energy and van der Waals energy dominated.

(3) The aggregated structure model of 20 bituminous coal molecules was constructed. After optimization by molecular mechanics and molecular dynamics simulations, the macromolecules in the aggregated structure model were restricted by surrounding molecules, and the original sheet-like aromatic carbon structure was approximately parallel. Distortion occurred, the lamellar structure was disordered, and the complete condensed matter structure model was compact. The coal had an occupied volume of 42025.14 Å$^3$, a pore volume of 6534.86 Å$^3$, and a surface area of 9985.43 Å$^2$. When the relative pressure of liquid nitrogen is 0.995, the adsorption capacity is 1.68 cc/g, which is 0.02 cc/g different from the established model, which verifies the accuracy of the model.

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Figure 11. Molecular aggregation state model and pore distribution of bituminous coal: (a) agglomeration model of coal, (b) aggregate state model and pore volume of coal, and (c) pore volume of coal.

Figure 12. Nitrogen adsorption and analytical curves.

![Image 1](image1.jpg)

![Image 2](image2.jpg)

![Image 3](image3.jpg)
Author Contributions

X.M. are contributed equally to this work.

Notes

The authors declare no competing financial interest.

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