



Application of Raman Spectroscopy in the Characterization of Coal Macromolecular Structure

Tian Wang

School of Resources & Environment, Henan Polytechnic University, Jiaozuo 454000, China

ABSTRACT

Raman spectroscopy is a rapidly developing rapid and non-destructive characterization technique for carbon materials in recent years, which has been widely applied to the characterization research of coal macromolecular structures. Through a systematic investigation, analysis, and summary of the research progress of Raman spectroscopy technology in the characterization of coal macromolecules at home and abroad, the following conclusions are obtained: (1) For the Raman spectroscopy testing of coal, processes such as boiling glue, polishing the sample, choosing different laser light sources, laser energies, and signal collection times will all have an impact on the Raman spectrum. Moreover, when performing peak fitting on the Raman spectrum, the coal rank of the sample and the structural information contained in the spectral peaks should be fully considered. (2) The influence of temperature on the structural evolution of organic matter in coal can be divided into two stages. Before graphitization, the Raman spectrum of coal shows irregular changes, while during the high-temperature graphitization process, the Raman disorder parameter gradually decreases. Under normal temperature and pressure conditions, the characteristic peaks of the Raman spectrum will shift linearly to a higher peak position, which is consistent with the response variation law of the Raman spectrum to stress. Additionally, the structural defects caused by tectonic stress will reduce the structural order of coal-measure graphite. (3) There is no strict corresponding relationship between the Raman spectrum disorder parameter and the coalification degree. Based on previous research results, it is believed that this may be closely related to factors such as the fact that the evolution of the order of coal macromolecular structures and the evolution of chemical structures are not completely synchronous, and that tectonic stress increases structural disorder by introducing structural defects. (4) Other applications of Raman spectroscopy in the characterization of coal structures include calculating the size of aromatic lamellae, the indicative significance of special peaks, and using the second-order Raman spectrum to characterize coal structure information. However, caution is still required during practical use.

KEYWORDS

Raman spectroscopy; Coal macromolecular structure; Peak fitting; Structural order; Coalification degree

1. INTRODUCTION

Coal is a special type of organic rock, mainly composed of C (with a mass fraction > 70%), followed by H, O, etc[1]. The main component of the organic matter in coal is a three-dimensional highly cross-linked amorphous macromolecular polymer. Each macromolecule is formed by the polymerization of many basic structural units with similar structures. In order to describe such a complex structure, scholars have proposed various coal macromolecular structure models. With the deepening of coalification, the coal rank gradually increases. Generally, the structure of coal shows the continuous detachment of lipid components and heteroatom functional groups, the continuous

improvement of the aromatization and condensation degree of condensed aromatic rings, and the continuous increase in the orientation and order level of aromatic lamellae[2]. Accurately depicting and quantitatively characterizing the structural characteristics of coal macromolecules can provide important information for exploring the mechanism of coal structure evolution.

Raman spectroscopy is a rapidly developing rapid and non-destructive characterization technique for carbon materials in recent years, which has been widely applied to the characterization research of coal macromolecular structures[3,4]. The Raman spectrum is usually divided into the first-order mode Raman (1000 - 1800 cm^{-1}) and the second-order mode Raman (2300 - 3100 cm^{-1}). Most of the research on the Raman spectrum of coal focuses on the spectral bands of the first-order mode, mainly including the D peak spectral band ($\sim 1350 \text{ cm}^{-1}$) and the G peak spectral band ($\sim 1580 \text{ cm}^{-1}$)[5]. For the macromolecular structure of coal, not only does the G peak shift to a higher frequency spectral band (usually located near 1600 cm^{-1}), but also a D peak appears at 1350 cm^{-1} . Since there is no D peak in a perfect graphite crystal, the D peak is often interpreted as a structural defect peak or a structural disorder peak. The physical meanings of the G peak and the D peak have been studied to a certain extent in the structures of graphite, graphene, and condensed aromatic hydrocarbons. The G peak is considered to originate from the E_{2g} symmetric vibration of sp^2 carbon atoms, and the D peak is considered to originate from the A_{1g} symmetric vibration of sp^2 carbon atoms[6-8]. Due to the complex macromolecular structure of coal, which is not a single structure, there is currently a lack of theoretical basis for the interpretation of the D peak and the G peak. Researchers mostly use the method of analogy with other carbon-containing materials or combine it with other means to achieve the purpose of analyzing the coal structure[9].

Based on the publicly available literature data in recent decades at home and abroad, this article systematically summarizes the problems that need to be paid attention to in the application of Raman spectroscopy in the characterization of coal macromolecular structures. The main contents include: (1) The problems that need to be paid attention to in the acquisition of Raman spectra and the process of peak fitting; (2) By discussing the application of Raman spectroscopy in the evolution process of the structural order of coal, the influences of factors such as temperature, confining pressure, and tectonic stress on the structural order of coal are analyzed; (3) Combined with the application of Raman spectroscopy in the characterization of coalification degree, the existing problems and possible reasons are analyzed; (4) Other applications of Raman spectroscopy in the characterization of coal structures are introduced, including calculating the size of aromatic lamellae, the indicative significance of special peaks, and using the second-order Raman spectrum to characterize coal structure information, etc. In addition, it also includes a small amount of research achievements on the Raman structural characterization of substances such as coke, kerogen, and shale organic matter, which have similar macromolecular structures to coal.

2. ACQUISITION OF RAMAN SPECTRA AND PEAK FITTING

2.1. Acquisition of Raman Spectra

The acquisition of Raman spectra is affected by various factors. The sample preparation method has a significant impact on the Raman spectrum. For example, boiling glue, polishing and grinding the coal sample can make the surface of the coal more flat[10], reduce the scattering and absorption of light, and thus improve the quality of the Raman signal. If the sample surface is rough, the light will undergo diffuse reflection on the sample surface, which will lead to the weakening of the Raman signal and the increase of noise, making the baseline of the spectrum unstable and the characteristic peaks unclear, which is not conducive to subsequent analysis[11].

The selection of the laser light source and laser energy is also crucial[12]. Different laser light sources have different wavelengths and powers, which will have different impacts on the Raman spectrum. For example, using a laser light source with a longer wavelength, due to its stronger penetration ability,

it can detect the information deeper inside the sample. For some coal samples with complex internal structures, it may be more conducive to obtaining a comprehensive Raman spectrum. However, at the same time, the Raman scattering cross-section of a long-wavelength laser is relatively small, which may lead to a weak signal intensity. If the laser energy is too high, it may cause a thermal effect on the sample, resulting in structural changes in the sample, and thus affecting the accuracy of the Raman spectrum. If the laser energy is too low, the signal intensity will be insufficient, which is also not conducive to the acquisition of the spectrum[13].

The signal collection time will also affect the quality of the Raman spectrum[14]. Appropriately extending the signal collection time can increase the number of photons received by the detector, improve the signal-to-noise ratio, and make it easier to detect weak peaks in the spectrum. However, if the signal collection time is too long, more environmental noise may be introduced. Moreover, for some unstable samples[15], long-term illumination may cause changes in the sample, which will instead reduce the reliability of the spectrum.

2.2. Problems Needing Attention in the Peak Fitting Process

Peak fitting is an important step in the analysis of Raman spectra. When performing peak fitting on the Raman spectrum of coal, the coal rank of the sample and the structural information contained in the spectral peaks need to be fully considered. The coal rank is different, and the macromolecular structures inside are also different, and the corresponding Raman spectral characteristics are also different. The structure of low-rank coal is relatively complex, containing more aliphatic side chains and functional groups. Its Raman spectrum may require fitting more peaks to describe its structural characteristics[16,17]. While the structure of high-rank coal is relatively simple, with a high degree of aromatization, and the number of fitted peaks is relatively small.

When selecting the fitting function, the Gaussian function and the Lorentz function are two commonly used functions. The Gaussian function is suitable for describing symmetric and relatively narrow peaks and is often used for the fitting of amorphous carbon materials. The Lorentz function is more suitable for describing wide and asymmetric peaks and is mostly used for the fitting of crystal and microcrystalline structure materials[18]. Due to the special structure of coal, which contains both amorphous carbon parts and microcrystalline structures, it may be necessary to select an appropriate function according to the actual situation or use a combined function of the two (such as the Voigt function) during fitting. During the fitting process, in order to improve the repeatability of the data, it is generally not necessary to fix the peak position and peak width. Only the number of peaks to be pre-fitted needs to be selected, and self-iterative calculation is carried out. In this way, the fitting result can be more in line with the actual spectral characteristics and avoid errors caused by artificially fixing parameters. However, at the same time, the iterative process needs to be reasonably controlled to ensure the convergence and stability of the fitting result.

3. APPLICATION OF RAMAN SPECTROSCOPY IN THE EVOLUTION PROCESS OF COAL STRUCTURE ORDER

3.1. Influence of Temperature

The influence of temperature on the structural evolution of organic matter in coal can be divided into two stages. Before graphitization, with the increase of temperature, the Raman spectrum of coal shows irregular changes[19]. This is because at lower temperatures, the organic matter in coal mainly undergoes some chemical reactions such as the decomposition and recombination of functional groups. These reactions are relatively complex and there is no obvious regularity, resulting in irregular changes in the Raman spectrum. For example, the aliphatic side chains in coal will break at a certain temperature, and small molecular gases will escape. At the same time, some cross-linking

reactions may occur between aromatic rings[20]. However, the degree and mode of these reactions are affected by many factors such as the initial structure of coal and the impurity content, making it difficult for the Raman spectrum to show a unified change trend.

During the high-temperature graphitization process, the Raman disorder parameter gradually decreases. With the continuous increase of temperature, the carbon atoms in coal gradually tend to be arranged orderly and transform into a graphite structure. Parameters such as the intensity ratio (ID/IG) and full width at half maximum of the D peak and G peak in the Raman spectrum can reflect this degree of order[21]. The smaller the ID/IG value, the more the structure of coal is close to the ordered structure of graphite. Because the D peak represents structural defects, the relative decrease of its intensity indicates a reduction in defects and an increase in structural order. Under the action of high temperature, the aromatic lamellae in coal gradually increase in size and are arranged more regularly, making the size of graphite microcrystals continuously increase, resulting in a decrease in the Raman disorder parameter.

3.2. Influence of Confining Pressure

Under normal temperature and pressure conditions, the characteristic peaks of the Raman spectrum will shift linearly to a higher peak position. This is because the action of confining pressure will compress the internal structure of coal, reduce the distance between molecules, and change the bond length and bond angle, thus leading to the displacement of the characteristic peaks of the Raman spectrum. For example, under the action of pressure, the interaction between aromatic rings in coal is enhanced, and the vibration frequency of the C-C bond changes, causing characteristic peaks such as the G peak to shift to a higher wavenumber direction[22,23]. This linear displacement relationship can be fitted through experimental data to establish a quantitative relationship between pressure and the displacement of the characteristic peaks of the Raman spectrum, providing a basis for studying the structural changes of coal reservoirs underground under different pressure conditions.

3.3. Influence of Tectonic Stress

Tectonic stress has a significant impact on the structural order of coal. The structural defects caused by tectonic stress will reduce the structural order of coal-measure graphite. When coal is affected by tectonic stress, defects such as dislocations and cracks will be generated inside, which will destroy the original ordered arrangement of coal macromolecules. It is manifested in the Raman spectrum as an increase in the intensity of the D peak and an increase in the ID/IG value, indicating an increase in structural defects and disorder. Moreover, different types of tectonic stress (such as shear stress, tensile stress, etc.) have different influence modes and degrees on the coal structure[24]. Shear stress may cause the dislocation of the layered structure of coal, forming more structural defects. Tensile stress may cause the breakage of chemical bonds in coal, also increasing the structural disorder. By analyzing the changes in the Raman spectrum under the action of tectonic stress, the tectonic history and stress environment experienced by coal can be inferred.

4. APPLICATION OF RAMAN SPECTROSCOPY IN THE CHARACTERIZATION OF COALIFICATION DEGREE

4.1. Relationship between Raman Spectrum Disorder Parameter and Coalification Degree

There is no strict corresponding relationship between the Raman spectrum disorder parameter and the coalification degree. Generally, it is believed that with the increase of the coalification degree, the structure of coal gradually tends to be ordered, and the Raman disorder parameter (such as ID/IG) should gradually decrease[25]. However, actual research has found that this is not always the case.

For example, in some coal samples, although the coalification degree has increased, the ID/IG value has not decreased significantly, or even increased. This may be related to a variety of factors.

4.2. Existing Problems and Possible Reasons

On the one hand, the evolution of the order of coal macromolecular structures and the evolution of chemical structures are not completely synchronous. In the coalification process, the changes in chemical structures (such as the detachment of aliphatic side chains and the condensation of aromatic rings)[26] and the changes in structural order (such as the orientation arrangement of aromatic lamellae and the increase in the size of microcrystals)[27] are interrelated but not completely consistent processes. At certain stages, the changes in chemical structures may dominate the characteristics of the Raman spectrum, and at this time, the influence of the changes in structural order on the Raman spectrum may be masked[28]. For example, when the coalification degree increases, although the condensation reaction of aromatic rings makes the chemical structure more stable, if a large number of structural defects are generated at the same time (possibly due to geological effects and other reasons), then the intensity of the D peak in the Raman spectrum may increase, resulting in an increase in the ID/IG value, which is inconsistent with the expected trend that the ID/IG value decreases with the increase of the coalification degree.

On the other hand, tectonic stress increases structural disorder by introducing structural defects. During the formation and evolution process of coal, it is often affected by various tectonic stresses. Tectonic stress will generate structural defects such as dislocations and cracks in coal, and these defects will significantly affect the characteristics of the Raman spectrum. Even if the coalification degree is increasing normally, if it is affected by strong tectonic stress and a large number of structural defects are generated, it will make the Raman spectrum show a high degree of disorder, thus interfering with the normal corresponding relationship between the Raman spectrum disorder parameter and the coalification degree.

5. OTHER APPLICATIONS OF RAMAN SPECTROSCOPY IN THE CHARACTERIZATION OF COAL STRUCTURES

5.1. Calculating the Size of Aromatic Lamellae

Raman spectroscopy can be used to calculate the size of aromatic lamellae in coal[29]. By analyzing some parameters of the D peak and G peak in the Raman spectrum, such as the peak intensity ratio and full width at half maximum, and combining with relevant theoretical models, the average size of the aromatic lamellae can be estimated. For example, according to the theory proposed by Tuinstra and Koenig, for carbon materials with a high degree of graphitization, there is a certain quantitative relationship between ID/IG and the average size L_a of the aromatic lamellae[30]. Although the structure of coal is more complex than that of an ideal graphitized material, this relationship can also be used to estimate the size of the aromatic lamellae to a certain extent[31]. The information on the size of the aromatic lamellae obtained through this method is helpful to deeply understand the structural characteristics of the coal macromolecules and the variation law of the structure during the coalification process.

5.2. Indicative Significance of Special Peaks

In the Raman spectrum of coal, in addition to the common D peak and G peak, some special peaks may also appear, and these special peaks have certain indicative significance. For example, in the Raman spectrum of some coal samples, a peak located around 1200 cm^{-1} may appear, and this peak may be related to certain specific functional groups or structural units in coal. Research has found that this peak may be related to the presence of more aliphatic side chains or some heteroatom groups

in coal[32,33]. Through the study of these special peaks, some special structural information in coal can be obtained, further enriching the understanding of the coal macromolecular structure. Moreover, the appearance or non-appearance of special peaks and the changes in their intensities may also be related to factors such as the metamorphic degree and origin of coal, providing more clues for studying the formation and evolution of coal.

5.3. Second-Order Raman Spectrum for Characterizing Coal Structure Information

The second-order Raman spectrum is the overtone and combination of the vibration of the first-order Raman spectrum. The second-order Raman spectrum of coal generally includes the 2D peak (2700 cm^{-1}), the D + G peak (2900 cm^{-1}), and the 2G peak (3200 cm^{-1}). For disordered carbon materials such as coal, the 2D peak can effectively characterize the C-C single bonds between aromatic rings. The 2G peak mainly corresponds to the number of graphene layers in highly ordered crystalline carbon structures such as graphite, and it can characterize the aromatic ring structure in coal. The D + G peak is a combination of the D peak and the G peak, which is usually attributed to the large-medium aromatic ring system in coal. It is generally believed that the second-order Raman spectrum is closely related to the c-axis order of the structure in coal[34,35]. By analyzing the intensity, position, and other information of each peak in the second-order Raman spectrum, more detailed information such as the arrangement mode of aromatic rings and the interlayer interaction in the coal structure can be obtained. However, it should be noted that when analyzing the second-order Raman spectrum, due to its relatively weak signal and being easily affected by factors such as noise, more careful data processing and result analysis are required.

6. CONCLUSION

Raman spectroscopy technology has important application value in the characterization of coal macromolecular structures. However, there are still some issues that need to be taken into consideration during practical applications. When obtaining Raman spectra, factors such as sample preparation, laser light source and energy, and signal collection time will all have an impact on the quality of the spectra. When performing peak fitting, the coal rank and the structural information of the spectral peaks should be fully considered, and the fitting function and parameters should be reasonably selected.

In the study of the evolution of the order of coal structures, temperature, confining pressure, and tectonic stress have different influence patterns on the Raman spectra of coal. There is no strict corresponding relationship between the disorder parameters of Raman spectra and the coalification degree, which is related to the asynchronous evolution of the order of coal macromolecular structures and the chemical structure evolution, as well as the structural defects introduced by tectonic stress.

In addition, Raman spectroscopy is also applied in calculating the size of aromatic lamellae, indicating special peaks, and characterizing the coal structure through second-order Raman spectra. However, the analysis results need to be treated with caution.

In the future, with the continuous development of technology and the deepening of research, Raman spectroscopy technology is expected to play a greater role in the field of coal macromolecular structure characterization, providing more accurate and comprehensive information for related research on coal.

CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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