



Structural characteristics of coal functional groups using quantum chemistry for quantification of infrared spectra



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ABSTRACT

The extinction coefficient differs for different functional groups making the quantitative analysis of their infrared spectra problematic. Although the coefficients of some functional groups have been researched previously, they are inaccurate because of deviations in techniques used and linear fitting. The distribution and structural characteristics of functional groups from coal infrared spectra is therefore inaccurate. In this study, quantum chemistry methods are used for the quantification of coal infrared spectra based on the Beer–Lambert law. The effect of the extinction coefficients of different functional groups is eliminated. The experimental infrared intensities, unit absorption intensities and their ratios are obtained to calculate the percentage composition of coal functional groups and molecular structure parameters. Accurate distribution and structural characteristics of coal functional groups are obtained. A linear relationship between the distribution of some functional groups and structural parameters is obtained. Multiple structural parameters are used to determine the grade and maturity of coal samples. The ethylene in coal oxidation experiments below 200 °C is consistent with the hydrocarbon-generating potential parameters. These results will improve the accuracy of the quantitative analysis of infrared spectra for determining coal structural features and provide an index for the utilization and prevention of the spontaneous combustion of coal.

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1. Introduction

Coal is one of the main energy sources in the world and is used as a raw material to produce natural gas and kerosene. The spontaneous combustion of coal may occur during its use, storage and transportation. A quantitative analysis of the distribution and structural characteristics of coal functional groups is important because spontaneous combustion is related to the active functional groups and molecular structure of coal.

Currently, analytical chemical techniques such as ^1H [1,2] and ^{13}C [3–5] nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FT-IR) [6–15] are used for determining the distribution and structural characteristics of coal functional groups. FT-IR is a simple and affordable technique. Painter [16–18] and Solomon [19,20] have quantified the abundance of coal functional groups and assigned particular bands to various functional groups. Orrego-Ruiz [10] quantified the molecular structure of coal from FT-IR information on the functional groups. FT-IR spectroscopy is applied widely to describe the characteristics of coal macerals [6,7,9,11–15]. From FT-IR studies of coal, differences between traditional FT-IR techniques, diffuse reflectance FT-IR (DRIFT), attenuated total reflectance (ATR) and photo acoustic (PAS) methods have been illustrated. Traditional FT-IR [16] techniques employ the KBr pellet methodology conducive to quantitative analysis, but samples

need to be well dispersed in the pellet. ATR spectroscopy [21] reduces sample preparation procedures and avoids the influence of KBr, but lacks a mathematical description for the quantitative interpretation of the spectra. PAS and DRIFT methods [22–24] can produce good quality infrared spectra for the quantitative analysis of coal functional groups, but PAS is demanding on the environment [25] while DRIFT is simpler.

The DRIFT spectrum is based on the Kubelka–Munk law [26], in agreement with the Beer–Lambert law [27,28] and is linearly proportional to the concentration and extinction coefficients of the functional groups in coal. Fuller and Griffiths [29] firstly applied DRIFT to coal and compared DRIFT and the Beer–Lambert spectrum to relate coal rank with functional group intensity. Ito [30,31] applied DRIFT to study the degree of coalification and carbonization of coal samples. The Gaussian fit and deconvolution are the first steps in the quantitative analysis of FT-IR spectra. Deconvoluted Gaussian spectra of coals by DRIFT were used to observe the absorption band variation of OH ($2700\text{--}3700\text{ cm}^{-1}$) and aromatic ($900\text{--}650\text{ cm}^{-1}$) groups by Kaihara et al. [32]. Christy et al. [33] studied the structure of asphaltenes and resins but their results are qualitative and semi-quantitative. Chen et al. [34] used deconvolution to determine the intensities of asphaltene FT-IR spectra. Sobkowiak and Painter [35] applied a Gaussian fit to confirm the stretching of the hydroxyl and C–H aliphatic groups in pyridine extracts from mineral coal. However, quantitative analysis of the coal spectra was not ideal because different functional groups have

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different extinction coefficients. Solomon and Carangelo [20] determined the extinction coefficients by the linear fitting of the spectral intensities of coal functional groups in distinct concentrations via traditional infrared performing technology. The extinction coefficients have since been used by Jorge et al. [10]. However, because of defects in traditional FT-IR and the heterogeneity of coal, experimental extinction coefficients determined in the quantitative analysis of coal sample spectra have large errors. Hence, the distribution and structural characteristics of the functional groups in coal are still unclear.

Quantum chemistry applies quantum mechanics to study molecular chemistry and to calculate the exact vibrations of molecular bonds. Considering the problems in the quantitative analysis of infrared spectra, quantum chemistry can be applied to build theoretical infrared spectra to analyze the molecular structure of complex organic components. Murgich et al. [36] have determined the physicochemical properties of asphaltene by molecular modelling. Quantum mechanical treatment software for calculating the dimensions and chemical properties of FT-IR spectra has been developed by Takanohashi et al. [37], Rogel [38] and Neugebauer et al. [39]. Quantum chemical calculations have been used to calculate the theoretical spectrum of asphaltenes by Coelho [40–42]. For example, the linear relationship [40] between the intensity ratios at 2927 and 2957 cm^{-1} for theoretical IR and experimental DRIFT spectra and the ratios $n\text{CH}_2/m\text{CH}_3$ in asphaltenes have been analyzed to calculate the molecular weight of the aliphatic chains. The same research has been applied for the functional sulfur chemical structure in asphaltenes [42]. He [41] obtained a reasonable linear correlation for the infrared intensities between the stretching (2900–3100 cm^{-1}) and out-of-plane deformation (700–900 cm^{-1}) of the aromatic region using theoretical spectra by quantum chemistry calculations and experimental infrared spectra. However, quantum chemistry methods have seldom been mentioned in previous research regarding quantitative analysis for the functional resolution of coal. Although a good linear relationship exists between quantum chemistry calculation spectra and experimental spectra, quantum chemistry calculation results have not been applied to revise the influence of differences in extinction coefficients for different functional groups in the quantitative analysis of experimental spectra. Therefore, the fundamentals and application of quantum chemistry may solve problems in the quantitative analysis of IR spectra for determining the distribution and structural characteristics of functional groups.

We use ratios of experimental and theoretical infrared intensity to analyze quantitatively the functional groups in coal. The influence of extinction coefficient on the quantitative analysis of infrared spectra based on the Beer–Lambert law is eliminated. Therefore, accurate distribution and structural characteristics of coal functional groups are obtained. A linear relationship is obtained between the contents of functional groups in coal and coal structural parameters. These results improve the accuracy of the quantitative analysis of infrared spectra, and allow

Table 2

Proximate analyses, heating, hydrogen and H/C of coal samples 0.04–0.075 mm in size.

Species	Proximate analyses (%)				Heating (kJ g^{-1})	Hydrogen (%)	H/C
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	$Q_{\text{net, ad}}$	H_{ad}	
BZ	9.86	20.65	30.01	34.08	21.81	4.49	0.79
LT	11.25	8.34	32.17	48.24	28.28	5.89	0.73
YM	12.15	6.82	33.67	47.36	29	4.79	0.61
CJS	5.82	8.58	28.74	56.86	30.03	5.28	0.56
SJS	4.99	6.8	32.21	59	29.04	5.31	0.55
JX	2.82	7.85	34.82	54.51	31.89	5.01	0.52
ZGZ	1.2	17.48	26.71	55.1	28.48	4.59	0.50
WG	1.27	20.82	23.29	54.62	26.88	4.28	0.47
WJD	1.37	15.2	24.49	58.94	27.41	4.91	0.45
YL	1.11	22.14	21.4	55.35	26.39	4.14	0.42
GQ	1.74	10.41	12.34	75.51	31.23	4.25	0.34
XF	0.94	13.67	10.11	64.1	25.29	3.42	0.32
XQ	0.95	14.47	12.04	72.54	29.679	3.64	0.30
KBL	0.52	7.46	11.76	80.86	32.93	3.78	0.27
BJG	0.41	2.26	8.81	88.52	33.07	3.75	0.25

for an active inhibition of functional groups and the chemical utilization of coal such as in catalytic hydrogenation. Molecular structure parameters provide information on maturity grade, hydrocarbon-generating potential and coal polymerization.

2. Samples and experiments

2.1. Sample characteristics

The fifteen Chinese coal samples used in this study (ages, mines, origins, vitrinite reflectance (R_o) and sample rank given in Table 1) were kept under an inert atmosphere. The samples were crushed using a hammer and ground with an agate mortar in a vacuum glove box under inert atmosphere, to produce a coal grain size of 0.04–0.075 mm. A glove box was used to prevent spontaneous combustion during grinding and possible structural and surface reactivity changes. Following grinding, samples were dried overnight under vacuum at 313 K. The proximate analyses, heating, hydrogen and the ratio of hydrogen and carbon (H/C) of the prepared samples are listed in Table 2.

2.2. Infrared spectrum experiments

Characteristics of the coal surface functional groups were recorded on a Nicolet 6700 Fourier transform infrared spectrometer by Nicolet in USA with wave number from 4000 to 650 cm^{-1} and resolution of 4 cm^{-1} . Pure ground KBr was used to obtain a reference spectrum. Approximately 4 mg of each dry coal sample was ground in an agate

Table 1Ages, mines, origins, vitrinite reflectance (R_o) and rank of coal samples 0.04–0.075 mm in size.

Species	Mine	Origin	Age	R_o (%)	Coal rank
BZ	Beizao	Shandong	Paleogene	0.37	Lignite B
LT	Liuta	Erdos Basin	Jurassic	0.43	Subbituminous
YM	Yima	Henan	Jurassic	0.47	Subbituminous
CJS	Chenjiashan	Shanxi	Jurassic	0.56	Bituminous D
SJS	Shanjiaoshu	Guizhou	Permo–Carboniferous	0.67	Bituminous C
JX	Jiaxiang	Shandong	Permo–Carboniferous	0.75	Bituminous C
ZGZ	Zhaogezhuang	Hebei	Permo–Carboniferous	0.83	Bituminous C
WG	Wugou	Anhui	Permo–Carboniferous	1.04	Bituminous B
WJD	Weijiadi	Gansu	Permo–Carboniferous	1.18	Bituminous B
YL	Yangliu	Anhui	Permo–Carboniferous	1.23	Bituminous B
GQ	Gequan	Hebei	Jurassic	1.35	Bituminous B
XF	Xinfeng	Henan	Permo–Carboniferous	1.77	Bituminous A
XQ	Xinqiao	Henan	Permo–Carboniferous	2.16	Anthracite C
KBL	Kabuliang	Ningxia	Permo–Carboniferous	2.29	Anthracite C
BJG	Baijigou	Ningxia	Permo–Carboniferous	2.35	Anthracite C

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