



Fine structure of Raman spectra in coals of different rank



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ABSTRACT

Fine structure of *G* and *D* bands in Raman spectra of various coals is studied. It is shown that the spectra of all sub-bituminous and bituminous coals can be decomposed into 5 subcomponents while the spectra of anthracites are best fitted using 2, 3 or 4 subcomponents depending on coal rank. The analysis enabled to separate one subcomponent of *D* band, probably responsible for imperfections in graphitic clusters, which shows nearly linear shift in the whole metamorphism range and can play role of the coal type indicator. We have found that Raman spectra of the same fat coal reveal one more subcomponent just before underground outburst and only two subcomponents after the outburst. This subcomponent near 1190 cm^{-1} is assignable to oscillations of methyl group bonds and probably can serve as the outburst indicator.

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1. Introduction

Raman spectroscopy relies on inelastic, rather than Rayleigh, scattering of visible, infrared, or ultraviolet photons on elementary excitations, yielding most direct information about vibrational modes of crystalline lattice. Although similar data can be obtained also by some other methods (e.g. neutron spectroscopy), Raman spectroscopy shows higher resolution, nondestructive nature, and easier specimen preparation. Moreover, micro-Raman spectroscopy offers advantages of sub-micron test volume that allows getting Raman images of a microstructure and collecting statistics from one specimen, and negligible interference from water. These features make Raman spectroscopy very promising technique for structural studies of crystalline, nanocrystalline, and amorphous materials including minerals (Gardiner, 1989).

These features are of primary interest in studying various carbon materials, which all are neither crystalline, nor completely amorphous. Tuinstra and Koenig (1970) were first who obtained Raman spectra of few carbon materials more than four decades ago, when the appropriate laser light sources became available. They had discovered that single crystals of graphite show one single band at 1575 cm^{-1} while the other carbon materials reveal one more line at 1355 cm^{-1} . The Raman intensity of the last band was found being inversely proportional to the crystallite size. These findings had implied that a very simple experimental technique for analysis of carbon materials could exist based on the relative band intensities ratio.

In order to check above idea, it was necessary to obtain the Raman spectra of coals as most disordered carbon materials being the starting

point in the graphitization sequence. Makovsky et al. (1971) first published such spectra, but Friedel and Carlson (1972) had presented data that are more exhaustive in short time. Surprisingly, they revealed in coals, activated carbons, and carbon black the same bands at about 1590 and 1360 cm^{-1} coinciding with the bands in transmission IR spectra. The authors called these bands *G*-band (graphitic) and *D*-band (disordered), respectively, and explained these results by degradation of coal samples under the laser beam.

However, subsequent works had confirmed the presence of *G* and *D*-bands in Raman spectra of all carbon materials except for crystalline graphite. Tsu et al. (1977) had found that Raman spectra of coals and disordered carbons are very similar. Nakamizo et al. (1974) had shown that *D*-band in glassy carbons becomes sharper and stronger with the increase in temperature of heat treatment up to $2000\text{ }^{\circ}\text{C}$. Bustin et al. (1995) had investigated effect of heating up to $900\text{ }^{\circ}\text{C}$ under high pressures up to 1.0 GPa on XRD, TEM and micro-Raman spectra of anthracite and a high volatile bituminous coal. They concluded that *D*-band remains in spectra even when other methods show generally complete graphitization. Nevertheless, Vidano and Fischbach (1978) had proved that the compression-annealed at $2950\text{ }^{\circ}\text{C}$ pyrolytic carbons reveals no *D*-band just as natural graphite. Pasteris and Wopenka (1991), who proposed to use presence or absence of *D*-band in micro-Raman spectra of graphite in various rocks as indicators of the rock metamorphism degree, subsequently confirmed this result.

Such discrete indicators were nevertheless only partial and labor-intensive solution. In attempt to discover some continuous regularity that could be put into base of a general precise method of characterization, two approaches were realized to the end of century, namely, more wide and/or detailed investigation of experimental Raman spectra and extension of a number of carbon materials involved into one work.

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Nakamizo et al. (1974) were apparently first who discovered a new wide line in natural graphite irradiated by a high power ruby laser. This line occurred at 2140 cm^{-1} in a higher wavenumber range unavailable in conventional measurements. Vidano and Fischbach (1978) had conducted a systematic study in this range called as second order spectrum as opposed to first order spectrum in the commonly used wavenumber range. They established that two new lines (G_1' and G_1'') arise at high enough temperatures of heat treatment (over $1400\text{ }^\circ\text{C}$) and grow up to $2600\text{ }^\circ\text{C}$ and that the G-band of the first order Raman spectrum can be decomposed into G and D' lines. The authors concluded that all three new lines exhibit monotonous dependence on the heat treatment temperature and hence can be used as indicators of graphitization degree. However, these findings related mainly to gas phase deposited carbon materials.

In order to extend series of carbon materials involved, Cuesta et al. (1994) had analyzed Raman spectra of 29 different carbon materials, starting from a subbituminous coal and ending by natural and synthetic graphite. Unfortunately, all correlations these authors presented were in fact self-correlations, i.e. correlations between different parameters or parameter combinations from the same spectra. For this reason, above materials only tentatively are recognizable in the metamorphism series. On the contrary, Wopenka and Pasteris (1993) had studied 37 carbonaceous rocks from kerogen and coals to graphite arranged along with geologically known metamorphism grade. However, plotted correlations revealed quite poor correlations. Beyssac et al. (2002) who studied Raman spectra of 54 sedimentary rocks had presented similar results. Correlations presented by these authors were better defined but generally non-monotonous.

Two conclusions derived from above mentioned earlier results were that the nature of the D-band stays essentially unknown (Reich and Thomsen, 2004) and that the parameters of Raman spectra can be used as indicators of artificial graphitization during high temperature treatment but not the natural metamorphism (Quirico et al., 2009). In this connection, most studies of the last decade were devoted to Raman spectra of naturally matured carbon materials, first of all coals.

As compared with other carbonaceous materials, coals have much more complicated structure determined largely by the coal maturing degree (Van Krevelen, 1993; Vandembroucke and Largeau, 2007). First relevant works of this period related to rocks or coals of one or few fixed metamorphism degrees rather than metamorphic series. Valentim et al. (2004) had shown that different coal macerals in the same coal specimen demonstrate micro-Raman spectra differing in band number and position. Guedes et al. (2005) had confirmed this conclusion for carbonaceous sedimentary rocks. They ascribed this effect to different organic precursors, as they graphitize to different extents under the same metamorphic conditions. Rodrigues et al. (2011, 2013) had traced the micro-Raman spectra evolution for individual coal particles with the temperature of high-temperature treatment. Above results comply with previous data and explain why a simple correlation between Raman spectra parameters and metamorphism degree is in fact unattainable (Potgieter-Vermaak et al., 2011).

Later attempts to establish such correlations were concentrated on coals and partially successful only within restricted ranges of metamorphic grade (Guo et al., 2008; Kwiecinska et al., 2010; Li, 2007; Li et al., 2006; Marques et al., 2009; Quirico et al., 2005). Potgieter-Vermaak et al. (2011) compiled up-to-date review of Raman spectroscopy application for the analysis of coal. Recent study of FTIR and Raman spectra parameters as functions of metamorphism degree defined as the vitrinite reflectance for China coals failed to reveal good correlations at all (Li et al., 2012). Nevertheless, Guedes et al. (2010) had found lately a quite good correlation between Penn State Coal Bank coals rank expressed as vitrinite reflectance and the integrated intensity ratio of the D-band to G-band.

However, the most promising up-to-date trend appears to be concerned the fine structure of Raman spectra in coals. Deconvolution of the D-band by fitting to a sum of Gaussian curves (D, D' and D'') was

first substantiated by Cuesta et al. (1994) for the case of activated carbons and some other amorphous carbon materials. The authors had supposed that the first two components at 1350 cm^{-1} and 1540 cm^{-1} are dependent of disorder (characterized as D and G-band intensity ratio) while the last component at 1335 cm^{-1} is independent of this parameter. Somewhat later Zheng and Chen (1995) had proposed the similar deconvolution for Raman spectrum of graphite contained in Chinese coals with a very small distance between components D_1 and D_2 at 1370 cm^{-1} and 1360 cm^{-1} respectively. The authors had assigned these lines to tectonic and thermal structural defects in graphite lattice, respectively.

Manoj and Kunjomana (2010) had shown that G-band in Fourier-transformed Raman spectra of bituminous and subbituminous Indian coals is dividable into two lines at 1580 cm^{-1} and 1605 cm^{-1} but the latter disappears or diminishes after leaching with HF. This fact indicates on the relation of the latter line with organic matter of coal. Finally, Sadezky et al. (2005) had published a detailed and statistically sound investigation of Raman microspectroscopy of soot and related carbonaceous materials, where they decomposed D-band into four Gaussians. From these, the D_1 line at 1350 cm^{-1} exhibited a pronounced dependence on the excitation laser wavelength that enabled to interpret it as a disordering parameter in accordance with X-ray measurements. The D_2 and D_3 lines at 1620 cm^{-1} and 1500 cm^{-1} respectively, being contained in the G-band, were independent of thermal treatment up to $800\text{ }^\circ\text{C}$ in vacuum and hardly could have been attributed to any structural imperfections. The D_4 line at 1180 cm^{-1} was observed only in soot but never in other carbon materials.

It follows from above brief review that a clear and unambiguous method of the first-order Raman spectra analysis is still the urgent problem. The aim of this work was to study the fine structure of such spectra for coals as a function of metamorphism degree.

2. Experimental

2.1. Materials

Coal samples originated from various mines of Donets Basin (Ukraine) so that to represent all ranks of bituminous coals and anthracites. Table 1 presents results of proximate and ultimate analysis performed in compliance with standards GOST R 53357-2009/ISO 17246:2005 and GOST R 53355-2009/ISO 17247:2005, respectively. Coal rank was determined using both former USSR's standard GOST 25543-88 now in force in Ukraine, based on the total carbon content, and ASTM D388 Vol. 05–06 (1991), based on primarily volatile content.

The specimen preparation sequence included coal lumps sampling directly during underground mining; immediate sealing the sample in closed air-proof bags, and storing therein until final treatment immediately before the measurements. The final treatment included smoothing one face of selected lumps by machining in order to obtain higher intensity of Raman scattering. To expose inner virgin layers of the material, we used a commonly known method of the sticky tape applying and sharp tearing off immediately before measurements. The rest lumps from the same bag served the base of standard proximate and ultimate analysis.

2.2. Raman spectroscopy

We used a Raman spectrometer with the blue excitation laser (Ciel, Eurolase) to record the first-order Raman spectra from smooth surface of so prepared coal specimens. Laser power was 17 mW per excitation spot with 2 mm diameter. The laser with wavelength 473 nm enabled to obtain the more intensive Raman scattering signal as opposed to red lasers with greater wavelengths and hence higher accuracy required to resolve fine structure of the spectra. Scattered light in the wavelength from 500 to 515 nm was collected at right angles by the recording system MORS 1/3648 (Troitsk, Russia) made

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