

ELECTRIC CHARGE REDISTRIBUTION INDUCED BY HYDROGEN BONDING IN LOW RANK COALS

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ABSTRACT

The nature of hydrogen bonds is predominantly electrostatic and strongly coupled to the environment in such a way, that formation or breaking of hydrogen bonds is accompanied by redistribution of electric charge among the participants. The intensity of infrared absorptions is related to charge separations along a particular bond. Therefore Fourier-Transform Infrared (FT-IR) spectroscopy is a promising tool to study the question whether charge separation in hydrogen bonding is important in coal. The objective of this study is to observe trends in infrared absorption intensities of hydrogen bonds, and in addition free OH and aliphatic deformation modes, as a function of moisture content in low rank coals, where hydrogen bonding is significant. FT-IR spectra of Zap lignite with varying moisture (0-22%) content were collected using the KBr pellet technique, and the spectra were curveresolved in the 3700-1900 cm^{-1} spectral region. The Mie theory of scattering was used for baseline correction and to calculate apparent density of coal particles. The data suggest that, in this particular lignite, charge redistribution as a result of hydrogen bonding is significant. It was observed that all of the measured quantities, i.e. the intensities of free OH, weak, medium and strong hydrogen bonds, aliphatic deformation modes as well as apparent density are influenced by the water monolayer buildup below 10% moisture, and that the direction of this influence reverses after saturation of the monolayer. A qualitative explanation of the charge redistribution mechanism involving polarization by hydrogen bond is given.

INTRODUCTION

Model calculations concerning quantitative aspects of hydrogen bonding in coal require that other noncovalent interactions, such as van der Waals forces, ionic and charge transfer type interactions, be more or less separable from hydrogen bonding. However, considering the nature of hydrogen bonds, this might not be true for coal. It is widely accepted that the nature of hydrogen bond is strongly electrostatic [1,2]. Consequently, the formation or breaking of hydrogen bonds is accompanied by redistribution of charge among the participants. Hydrogen bonds are also strongly coupled to the environment. For example, it was shown that in polypeptide chains hydrogen bonding and π - π stacking reinforce each other [3]. Quantum mechanical calculations reveal that a small change in the interaction potential originating from the vicinity of the hydrogen bond may lead to large-scale change in the bonding [4,5]. This interaction may be enhanced by the cooperative behavior of certain electric charges in coal. As a result this charge redistribution may well be extended beyond the participating coal molecules. Perhaps a good example of this is that coal can sustain and stabilize free electrons by delocalization along a larger condensed aromatic segment. Moreover, Flowers and coworkers [6] reported that the electron transfer to coal was a bulk property. If secondary effects of hydrogen bonding in coal are significant, it concerns important aspects of volumetric swelling theories like the separation of physical intermolecular interactions from hydrogen bonding interactions [7,8], and also dynamic properties of hydrogen bonding [8]. Another question is whether coal swelling can properly differentiate between free and hydrogen bonded OH functionalities [9] and/or inter and intramolecular hydrogen bonds. Since the intensity of infrared absorptions are related to charge separations along a particular bond, infrared spectroscopy seems to be a suitable tool to study this question. As a bonus to this approach, the apparent density of the coal particles can be calculated by applying Mie theory of scattering on the infrared spectra [10]. Water is natural to the coal structure and it was assumed that its presence in varying concentrations would invoke gradual changes in hydrogen bonding. A low rank coal (Zap lignite, Argonne Premium Coal Bank) was chosen in this work to study this question because of its capability to absorb significant amounts (up to about 26%) of moisture.

EXPERIMENTAL

The Zap lignite was dried in vacuum oven for 24 hours at 107 $^{\circ}\text{C}$ to decrease the moisture content to about 1.5%. The residual moisture was estimated by the TG-FT-IR technique [11]. The samples with varying moisture content were prepared by mixing wet (26%) and dried (1.5%) samples, and equilibrating them in sealed vials for one month. Fourier Transform Infrared (FT-IR) spectra were collected using the KBr pellet technique [12]. It was found that the

moisture equilibration between the coal particles and KBr at room temperature was very slow. However, at 107 °C in vacuum the moisture content of the coal particles in the KBr pellet could be decreased below 1.5%. A typical coal spectrum is shown in Fig.1. The sloping baseline is the result of light scattered by coal particles, and it can be corrected using the Mie theory [10] where the adjustable parameters are n (index of refraction), D (average particle size, μm) and d (particle density, g/cc). There are two regions with only scattering (above 3700 cm^{-1} and between $1800 - 1900\text{ cm}^{-1}$) to occur and scattering vanishes below $\approx 800\text{ cm}^{-1}$. Therefore the values of the d , n , and D could be determined iteratively through minimizing the integral functions

$$\int (I_{\text{Mie}}(d, n, D) - I_{\text{Spectr.}}) d(d, n, D) \quad 1.$$

All three adjustable parameters are known [10] to fall between $1 \leq d, n, D \leq 2$, I is the sum of adsorbances in the $3700\text{--}4500$ and $1800\text{--}1900\text{ cm}^{-1}$ region for the calculated (Mie) and measured (Spectr.) spectra with $I_{\text{Mie}} = 0$ below 800 cm^{-1} . The errors of the adjustable parameters, Δd , Δn and ΔD , were obtained through setting $\Delta d = 0.05$, and then estimating the corresponding errors of n and D ($\Delta n = 0.01$ and $\Delta D = 0.01$). This approach is valid, because the fit with the d , n , D parameters is excellent. n and D was constant within the error bar for all samples with $n=1.64$ and $D=1.50$.

The baseline-corrected spectrum of the 1.5% moisture sample is shown in Fig.1. It is also seen from this figure, that the pellet drying of this sample resulted in decreased hydrogen bond band intensities ($3600\text{--}3000\text{ cm}^{-1}$ region) but significantly increased the scattering. The additional scattering occurred on microcracks in the KBr pellet as a result of pellet drying. Therefore the Mie theory is not applicable to dried pellet samples without proper modifications. A rectilinear baseline correction [12] approximation was used in this particular case.

The conventional spectral deconvolution techniques usually fail if applied to spectra with highly overlapping bands [13,14]. An alternative approach used in this work is to choose available literature band assignments as the input parameters for the active IR bands in the $3700\text{--}1900\text{ cm}^{-1}$ spectral envelope. The input band positions were: free OH (3618 cm^{-1}) [15], weak (3560 ; 3495 cm^{-1}), medium (3450 ; 3409 ; 3300 ; 3204 ; 3122 cm^{-1}) [14-19] and strong hydrogen bonds (2741 ; 2555 ; 2372 ; 2215 ; 2043 ; 1902 cm^{-1}) [20], aromatic stretching vibrations (3040 cm^{-1}) [20] and aliphatic stretching and deformations (2960 ; 2935 ; 2900 ; 2870 ; 2840 cm^{-1}) [20,21]. The aromatic and strong hydrogen bond bands were broadband (bandwidths in the 100 cm^{-1} order) contributions, and the band shapes were Voigt functions [21]. The final band positions and shapes can be optimized by the curve-resolving routine (Spectra Calc., Galactic Ind.), but curve-resolving does not work well if narrow and broad bands overlap, which is the case for the aliphatic modes as seen in Fig.1. (between 3000 cm^{-1} and 2800 cm^{-1}). Therefore, the aliphatic absorptions were stripped off from the spectra and the two spectral fragments were curve-resolved separately.

RESULTS AND DISCUSSION.

Infrared intensity data. The total line intensity of a given $i \rightarrow j$ vibrational transition can simply be given as

$$I_{i,j} = \frac{h\nu}{3c} [(\mu_x^{(i)})^2 + (\mu_y^{(i)})^2 + (\mu_z^{(i)})^2] \quad 2.$$

where N is the Avogadro number, c is the speed of light and $\mu_{x,y,z}^{(i)}$ are the coefficients of the normal coordinate Q_k in the expansion of the electric moment

$$\mu_x = \mu_x^0 + \sum_{k=1}^{3N-6} \mu_x^{(k)} Q_k + \text{higher terms} \quad 3.$$

where the higher terms are thought to be small. The same can be written for the y and z components. The x component of the electric moment possessed by the molecule in its equilibrium position, μ_x^0 , is practically equal to the x component of the permanent electric moment and only vibrations that cause change in the electric moment are IR active. Since almost every molecule possesses sufficient symmetry, practically only one of the x, y, z components is different from zero. IR absorption of an intermolecular bond of the type $A - A$ may vanish because no dipole is generated by the vibration, but the IR absorptions in intramolecular hydrogen bonds may also vanish in molecules possessing sufficient conjugation in the vicinity of the hydrogen bond [22]. The same reduction occurs in stretching intensities of CH_3 , CH_2 and CH groups adjacent to double bonds [23]. Thus, the weakness of the IR intensity of a particular band is not necessarily connected with symmetry. Rather, charge transfer or conjugation compensates dipoles induced by the vibration. For this reason, trends in hydrogen bond and aliphatic stretching mode intensity changes can reflect charge redistribution in highly unsaturated materials like coal. On the contrary, free (non hydrogen-bonded) OH intensity is fairly proportional to the free OH concentration and is less effected by conjugation. It was found, that in lignites with increasing moisture content first a water monolayer is formed which is saturated at around 10% water [24,25]. Then a simple scenario for the coal macromolecule can be

described as follows. If water is added, the specific sites of the molecule will form hydrogen bonds with water, and the sites may be either hydrogen donor or acceptors depending on the electronegativity difference between water and the macromolecule. After the monolayer is filled up, hydrogen bonding between the second and first layer of water decreases the actual donor or acceptor character of the first layer, thereby changing the trend of charge transfer between water and coal as further water molecules are added. However, in heterogeneous complex aggregates like coal, these trends might be scrambled. The results are summarized in Table 1, and it is seen that samples with around 10% moisture are indeed distinct.

The free OH concentration is very low below 1.5% and it is maximum at 1.5% moisture. As a result of hydrogen bond formation with water, the free OH gradually decreases with filling up the water monolayer. Glass and Larsen [26] also observed the reaction of free OH with a number of organic bases. Free OH in coal can be stabilized sterically if there is no reacting partner in the immediate vicinity to form a hydrogen bond, or an existing hydrogen bond can be destabilized to form free OH through polarization by neighbors [5]. If the diminishing IR intensities below 1.5% water (see Table 1) were caused by partial decomposition of OH groups or other functionalities, it would not decrease significantly the free OH concentration, because the remaining OH groups will have an increased chance to remain free from interacting neighbors. A more suitable mechanism is intramolecular hydrogen bond formation coupled with increased conjugation. This supports a coal swelling model proposed by Painter and coworkers [27,28]. According to the model, the swelling of coal is associated with topological reorganization of the network rather than changing chain dimensions. Favoring intramolecular hydrogen bonding requires special folding of the macromolecules of which plenty of examples, especially among helical structures, exists in nature.

The change of aliphatic intensities (see Table 1.) as a function of water content is a proof, that the charge transfer as a result of hydrogen bond formation with water extends to, at least, a larger section of the coal molecule being involved in the hydrogen bonding. An intensity minimum was observed at around the monolayer saturation. The aliphatic stretching intensities decrease with electron transfer towards the aliphatic functionalities. With hydrogen bond formation the electron density increases at the donor site. Therefore a qualitative explanation is that the coal is the donor in the hydrogen bond with water.

The reduction, rather than the increase, of hydrogen bond intensities with the water monolayer buildup can also be related to the water monolayer buildup. As additional hydrogen bonds are formed, the donor strength of coal is decreased reducing the electronegativity difference between coal and water and increasing the symmetry of the hydrogen bonds.

Apparent density data. Fig. 2 shows the calculated apparent (or particle) densities as a function of moisture. Using the linear relationship established by Suuberg and coworkers [29] for the swelling of Zap lignite with water, the proportional decrease of apparent density with moisture content can be predicted. The same trend is expected from comparing the true (He) density (1.55 g/cc) [30] with water density (1.31 gr/cc, measured in our lab). Note, that the "water density" which is the true density of coal saturated with water (in place of He), is an approximation of the apparent density of water saturated coal. The apparent "swelling" densities in Fig.2 were calculated from the linear relationship (Suuberg) by normalizing the actual value at 1.5% moisture to 1.09, which is the average "Mie" density between 1.5 and 10% water. It is seen that, while the apparent "Mie" density is identical with the "swelling density at 1.5 and 21.8% water content, the change with water is not gradual, but rather abrupt at the monolayer saturation point. It is possible, that this is due to the particle size difference between the two type of experiment. The size of coal particles in the KBr pellets was 1.5 μm , therefore the presence of macropores larger than about half of that ($\approx 0.6 \mu\text{m}$) could be excluded. If the ratio of larger than $\approx 0.6 \mu\text{m}$ pores abruptly changes after the monolayer fill-up, this would explain the discrepancy between the scattering and macroscopic measurement techniques.

CONCLUSIONS

Infrared absorption intensities in the 3700-1900 cm^{-1} spectral region have been measured as a function of moisture in Zap lignite. The trends in absorption intensity changes as a function of moisture content can be related to water monolayer and subsequent secondary layer buildup. The polarization of hydrogen bonds changes direction at the monolayer saturation ($\approx 10\%$ water). These data suggest that the electric charge redistribution resulting from hydrogen bond formation and/or breaking in low rank coals is significant.

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Table 1. Infrared intensities. Peak areas, arbitrary units.

wt% water	Partial sum of hydrogen bonds				Aliphatic		
	Free OH*	Weak**	Medium**	Strong**	CH ₃ *	CH ₂ *	CH*
< 1.5	0	7.1	55.0	46.1	1.5	4.3	2.1
1.5	11.8	36.8	133.7	66.0	1.6	4.9	1.9
4.3	10.2	45.7	131.1	148.4	1.8	4.8	1.9
8.9	9.2	44.9	125.5	62.9	0.7	3.8	1.2
10.3	5.2	20.3	93.3	63.8	1.4	3.5	1.7
16.2	5.8	31.8	95.9	53.1	1.7	4.6	2.0
21.8	2.2	11.3	85.9	12.2	2.3	5.1	2.6

* Dry coal basis

** Wet coal basis

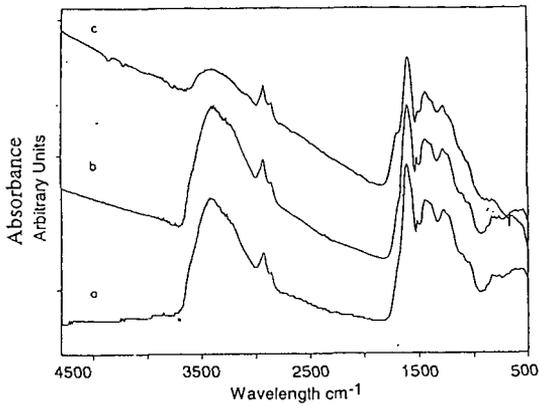


Figure 1. FT-IR spectra of Zap (1.5% moisture) a) after baseline correction; b) before pellet drying; and c) after pellet drying.

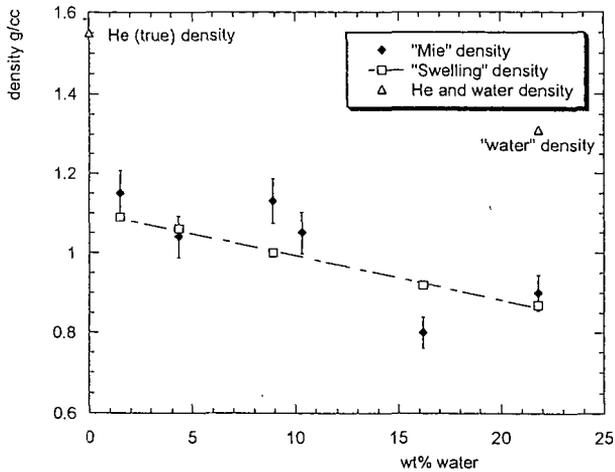


Figure 2. Comparison of calculated apparent densities. The "swelling" densities were derived from literature swelling data (Suuberg et.al. [29]) and normalized to 1.09 at 1.5% moisture, while the "Mie" density was calculated from FT-IR scattering data using the Mie theory of scattering and the KBr pellet technique. In addition the true (He) density [30] (dry coal) together with the water density (wet coal) is also shown.