

Estimation of Hydrogen Bond Distribution in Coal through the Analysis of OH Stretching Bands in Diffuse Reflectance Infrared Spectrum Measured by in-Situ Technique

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A new method was presented to estimate the strength distribution of hydrogen bonds in coal. The hydrogen bonds include the coal intramolecule hydrogen bonds and coal–water hydrogen bonds formed by hydroxyls in coal. The method analyzes the FTIR spectrum ranging from 2400 to 3700 cm^{-1} obtained using the in-situ diffuse reflectance IR Fourier transform (DRIFT) technique with neat, undiluted, coal samples. The FTIR spectra during the heat-up of eight coals (seven Argonne premium coals and an Australian brown coal), an ion-exchange resin, and a lignin were measured every 20 °C from room temperature to 300 °C. Each spectrum was divided into six hydrogen-bonded absorption bands by a curve-resolving method, then the amount of hydroxyls contributing to each hydrogen bond was estimated by Beer's law by using different absorptivity for each band. The strength of each hydrogen bond was estimated using a relation presented by Drago et al. that is known as one of the "linear enthalpy–spectroscopic shift relations". Using this analysis method, changes in hydrogen bond distributions (HBD) with increasing temperature were successfully estimated for all the samples examined. By utilizing the HBD the changes in enthalpies associated with the desorption of adsorbed water, the glass transition, and the decomposition of COOH groups were well estimated. Only FTIR spectra measurements were found to be enough to obtain such enthalpies. This greatly simplified the calculation procedure and increased the accuracy of the enthalpies. The validity of the proposed in situ FTIR measurement method and the analysis method for obtaining HBD was well clarified.

Introduction

It is believed that five associative interactions exist in coals.¹ These are covalent bonds, ionic linkages, hydrogen bonds, van der Waals forces, and π – π interactions. Of the five associative interactions hydrogen bonds, one of noncovalent associative interactions, are believed to play a key role to keep the macromolecular structure of low rank coals,^{1–7} and hence utilization of the low rank coals is significantly affected by the hydrogen bonding. Since a large amount of water is retained in the lower rank coal due to the hydrogen bonds, drying is one of drawbacks for the utilization of the coal. Hydrogen-bonded carboxylic and hydroxylic

groups in the coal cross-link at the early stage of pyrolysis, which affects significantly the subsequent main pyrolysis reactions.⁸ Usually the cross-linking reactions suppress the formation of volatiles. In solvent extraction of coal and/or the liquefaction of coal the interactions of coal surface and solvents play a crucial role. From a fundamental viewpoint, physical properties such as the glass transition temperature are significantly affected by the existence of hydrogen bonds. Therefore it is very important to quantify the hydrogen bonds in coal from both practical and fundamental viewpoints. Quantification means the estimation of the amount and the strength of each hydrogen bond.

Several attempts have been made to estimate the hydrogen bonds in coal using various methods, including solvent swelling phenomenon of coal, DSC, NMR, and FTIR. Experiments and analyses of solvent swelling of coal have been performed in relation to the role of noncovalent bonds in coal. One of the pioneer works is the one performed by Sanada and Honda.⁹ They have estimated the density of cross-links and the mean molecular weight between two adjacent cross-links by applying the Flory-Rehler theory for polymers to the

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swelling of coal by pyridine vapor. Since this pioneer work, many works have been presented and they have contributed to clarify the coal structure. Recently Larsen et al., for example, have presented a method to estimate the number of hydrogen-bond cross-links in coal by utilizing the swelling of coal with polar solvent diluted by nonpolar solvent.¹⁰ This method clarified that there are about 1.7 hydrogen-bond cross-links per 100 carbons in Illinois No. 6 coal and 0.3 hydrogen-bond cross-links per 100 carbons in Pittsburgh No. 8 coal. However, no information has been given on the strength distribution of hydrogen bonds in coal from solvent swelling examinations.

Direct or indirect estimation of heat accompanying the formation or disruption of hydrogen bonds is another method to estimate the strength of hydrogen bonds. Lucht et al.,¹¹ Mackinnon et al.,¹² and Yun et al.,¹³ for example, examined the glass transition of coal by the DSC measurement. Mackinnon et al. observed the second-order phase glass transition at around 110 °C during the heating of various coals. However, direct calorimetric measurements have been in general not successful, because many factors have to be taken into account to convert the experimentally obtained heat into the strength of hydrogen bonds.

Heats of wetting of coal in solvents such as water, methanol, etc., have been measured calorimetrically to elucidate oxygen functional groups in coal. As early as in 1957 Iyenger and Lahiri tried to correlate the heat of wetting and the energy of hydrogen bonding between coal oxygen functional groups and methanol.¹⁴ To calculate the energy of hydrogen bonds, they assumed that each COOH group is capable of hydrogen bonding with two CH₃OH molecules and that OH and C=O groups are each capable of hydrogen bonding with one CH₃OH molecule, respectively, and assigned the following hydrogen bond energy value for each hydrogen bond formed by these functional groups: COOH: 8.2 kcal/mol, C=O: 7.0 kcal/mol, and OH: 6.2 kcal/mol.¹⁵ By further assuming that all C=O groups are either chelated or interlocked with their corresponding number of OH groups and therefore not available for hydrogen bonding with water, which was deduced from the strong IR absorption band near 1600 cm⁻¹ in all coals, they found a remarkable statistical agreement between the heat of wetting and the total energy of hydrogen bonding calculated from the amount of oxygen functional groups and the hydrogen bond energies given above. Similar correlations were obtained for the heats of wetting in water and chlorobenzene and corresponding hydrogen bond energies, where the hydrogen bond energies for OH...O and OH...Cl were, respectively, assumed to be 4.5 and 3.9 kcal/mol. These pioneer works are very interesting in the sense that they related the hydrogen bonding energy to a directly measurable quantity, heat of wetting, although it may be questionable if their interpretation is correct.

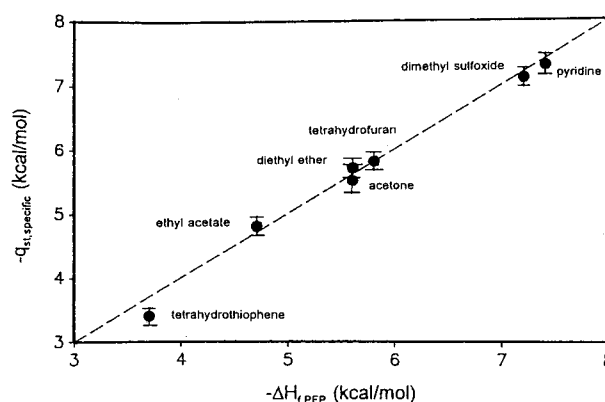


Figure 1. Specific adsorption enthalpy, $q_{st,specific}$, on demineralized Illinois No. 6 coal vs heat of hydrogen bond formation with *p*-fluorophenol, $\Delta H_{f,PPF}$, for seven bases.¹⁷

One of the indirect methods for the estimation of heat associated with a hydrogen bond is the estimation of isosteric adsorption enthalpy (heat of adsorption) from the adsorption isobars. Allardice and Evans estimated the heat of adsorption of water during the course of desorption of water from a raw brown coal.¹⁶ It increased from the level of heat of vaporization (43.88 kJ/mol-H₂O at 25 °C) to 60 kJ/mol-H₂O with the decrease of the amount of water adsorbed. This showed that coal has different adsorption sites for water; in other words, coal oxygen functional groups have different hydrogen bonding abilities. When the heat of adsorption was estimated from the readsorption isobars for the dried coal, on the other hand, its value was almost the same as the heat of vaporization irrespective of the amount of water adsorbed. This result shows that most of the hydrogen bonds formed among the oxygen functional groups in the dried coal are stronger than the hydrogen bonds that can be formed between the oxygen functional groups and water. This shows that the strength of hydrogen bonds in the dried coal cannot be estimated from water adsorption data. To overcome this drawback, Glass and Larsen presented a method to separate the heats of adsorption of organic bases on coal into non-specific and specific interactions.¹⁷ The specific interaction heats, $-q_{st,specific}$, which are judged to be the interactive energies between the bases and coal oxygen functional groups, are found to be equal to the heats of hydrogen bond formation between those bases and *p*-fluorophenol in liquid phase,¹⁸ $-\Delta H_{f,PPF}$, as shown in Figure 1. This clarified that the base-coal interaction and base-phenol interaction in the liquid phase can be treated in the same way. This analysis method would present a possibility to estimate the strength distribution of hydrogen bonds in coal by changing the bases systematically.

Infrared (IR) spectroscopy is surely one of the most promising methods to quantify the hydrogen bonds in coal directly.^{19–29} As Painter et al. reviewed,²¹ Fourier transform infrared spectroscopy with on-line microcom-

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puters has opened a new era of IR spectrometry. It has become a routine work to measure IR spectra and to manipulate them by spectral subtraction, curve resolving, factor analysis, etc., which lead the IR spectroscopy to a quantitative analysis method. However, there are several problems to be solved to apply the FTIR method to quantitative analysis of coal. The most commonly employed sample preparation method is the so-called KBr pellet method. A small amount of coal (1 to 3 wt %) is mixed with KBr powders, and they are pelletized to a transparent disk that is served to transmittance IR measurement. It is essential to grind both coal particles and KBr particles into the size less than the wavelength of the IR radiation. The most severe difficulty is the ubiquitous presence of water. It seems to be almost impossible to remove water effectively, especially when we intend to estimate the amount of OH groups from the OH stretching absorption bands around 3000 to 3600 cm^{-1} , since strong and broad water adsorption bands appear in the region. It is also very difficult to do subtractions of spectra on a 1/1 basis to obtain a difference spectrum without proper internal standards, because it is impossible to prepare two disks under identical conditions.

Overcoming these problems, Solomon et al. tried to quantitatively estimate the amounts of OH,²³ aliphatic hydrogen, and aromatic hydrogen³⁰ using the KBr pellet method in a series of works where careful sample preparation and elaborate data analysis were performed. It is reported that drying the KBr pellet for 48 h at 105 °C is enough to eliminate KBr–H₂O bands and that the absorptivity at 3200 cm^{-1} correlates very well with the total amount of OH irrespective of coal rank. On the other hand, the absorptivities for aliphatic hydrogen, a_{al} , and aromatic hydrogen, a_{ar} , were found to be coal rank dependent. Their values estimated, respectively, from the sets of peaks near 2900 cm^{-1} and near 800 cm^{-1} were $a_{\text{al}} = 746$ and $a_{\text{ar}} = 686$ for bituminous coals and $a_{\text{al}} = 710$ and $a_{\text{ar}} = 541$ for subbituminous coals and lignites in units of $\text{mg}^{-1} \text{cm}^{-2}$.

Solomon et al. tried to estimate the amount of OH directly from the OH stretch region to simplify the estimation, Painter et al. proposed to measure the spectrum ranging from 1550 to 1900 cm^{-1} of the acetylated coal for the estimation of OH amount.²⁴ By this method acetylated phenolic OH, alkyl OH, and NH groups were estimated from the bands of 1770, 1740, and 1670 cm^{-1} , respectively. This method was employed

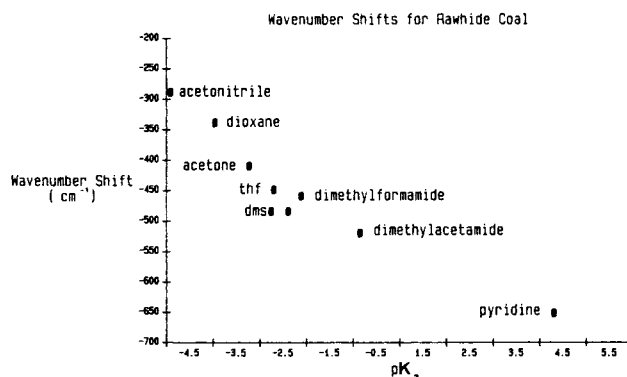


Figure 2. Plot of frequency shift of the O–H stretching band of Rawhide coal vs base strength of the adsorbed solvent.³¹

to overcome a number of problems associated with the use of the absorption band near 3400 cm^{-1} as a direct measure of OH group content. The main problems are water adsorption by the KBr matrix, water bound to coal in a complex manner, and the presence of more than one band in this region of the spectrum. These factors were judged to conspire to make quantitative measurements based on the 3400 cm^{-1} band suspect. This work and the work performed by Sobkobiak et al.²⁸ showed that the KBr pellet method is valid and precise when analyzing the bands except 3000 to 3600 cm^{-1} .

There are several problems to quantify the absorption bands near 3400 cm^{-1} as stated above, but the absorption bands ranging from 2400 to 3600 cm^{-1} contain important information on OH group associated hydrogen bonds. Fuller and Smyrl²⁵ showed that the in-situ diffuse reflectance IR Fourier transform (DRIFT) technique with neat, undiluted, coal samples can be well utilized to trace the in-situ reactions such as oxidation, dehydration, etc.²² This technique seemed to resolve most of the problems associated with the KBr pellet method: no sloping baseline appears; water adsorption by KBr does not occur; it is very easy to do subtractions of spectra on a 1/1 basis to obtain a difference spectrum. Analyzing difference spectra obtained by this technique, Fuller and Smyrl clarified the attributions of the absorption bands ranging from 2800 to 3625 cm^{-1} as follows—3625 cm^{-1} : weakly hydrogen bonded entities; 3540, 3390, 3290 cm^{-1} : structural difference and various types of hydrogen bonds; 2850–3000 cm^{-1} : aliphatic hydrogen; 3000–3100 cm^{-1} : aromatic hydrogen.

Larsen and Baskar related the strength of coal–solvent interactions with the most direct spectroscopic probe available: changes in the hydroxyl stretching frequency on hydrogen bond formation.³¹ The spectrum of vacuum-dried coal mixed with KBr was measured using a controlled-atmosphere cell by the DRIFT technique. The coal was then exposed to deuterated solvent vapor, and the spectrum of the coal adsorbing the solvent was measured. The value of the OH stretching frequency shift was estimated from the difference spectrum of the two spectra. Figure 2 shows the wavenumber shift against the pK_a value of the solvents (bases) used. The linear relationship was similar to that obtained when similar bases form hydrogen bonds to phenol in liquid phase. The good correlation in Figure 2 shows that this technique holds the promise of

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providing quantitative information of relative hydrogen bond strengths.

Painter et al.²⁶ reviewed a wealth of literature concerning hydrogen bonds, and attempted to define explicitly the types of hydrogen-structure present. They clarified that the functional groups present in coals are capable of forming hydrogen bonds with various acceptor groups are hydroxyls, and phenolic and carboxylic acids, and assigned the OH stretching frequency bands to the following hydrogen bonds—3611 cm⁻¹: free OH groups; 3516 cm⁻¹: OH- π hydrogen bonds; 3400 cm⁻¹: self-associated *n*-mers (*n* > 3); 3300 cm⁻¹: OH-ether O hydrogen bonds; 3200 cm⁻¹: tightly bound cyclic OH tetramers; 2800–3100 cm⁻¹: OH-N (acid/base structures).

Existences of the bands were determined by a curve-resolving method based on the second derivative of the spectrum and the eye and brain examination. The OH- π hydrogen bonds are judged partly to be due to OH groups that sterically cannot find an energetically preferable partner. This implicitly meant that very few OH groups exist as free OH. They also clarified that the frequency shifts from that of the free OH and the intensities of the bands provide fundamental parameters that can be used to determine structural characteristics such as bond lengths and the enthalpy of bond formation, although they did not estimate them.

As briefly reviewed, it has been clarified that there are several types of hydrogen bonds in coal, and that their existences are most vividly shown by the OH stretch frequency shift of IR absorption bands. However, no definite methods have been presented to estimate the strength distribution of hydrogen bonds, probably because of the difficulty in analyzing the OH stretch frequency bands associated with water bound to coal in a complex manner and the presence of more than one band in the region of the spectrum. If the KBr pellet method was employed, water adsorption by the KBr matrix should also be taken into account.

Apart from coal hydrogen bonds there have been a wealth of works on various hydrogen bonds, including various reviews and several books.^{32–34} In liquid-phase hydrogen-bonded adduct formation reactions between the OH functional groups of phenols and/or alcohols and various bases have been examined in detail using FTIR and thermodynamic considerations. The reaction for a phenol, for example, is represented by the following stoichiometric equation:



where Ph-OH \cdots B represents the hydrogen-bonded adduct, and ΔH is the enthalpy change of the reaction. The ΔH values for various combinations of phenols and bases were estimated by applying the van't Hoff equation to the equilibrium constants measured. The amount of hydrogen bonds is also obtained in the course of the measurement of equilibrium concentrations. When the hydrogen bond is formed, the IR wavenumber of the

O-H stretching vibration of the phenol shifts to a low wavenumber and generates heat ($\Delta H < 0$). The relationships between the enthalpy change, ΔH , and the OH wavenumber shift, $\Delta\nu_{\text{OH}}$, were examined for various phenol-base and alcohol-base combinations^{18,35–39}, and a linear relation was found to hold between ΔH and $\Delta\nu_{\text{OH}}$ by many investigators.^{38,40} The relationship is well-known as “linear enthalpy-spectroscopic shift relations”. The relationship obtained by Drago et al.,³⁸ for example, from many measurements is given by

$$-\Delta H = 0.067 \Delta\nu_{\text{OH}} + 2.64 [\text{kJ/mol}] \quad (2)$$

The values of $-\Delta H$ were interpreted as the strength of hydrogen bond by many investigators.^{10–13} However, Drago et al. thought that ΔH consists of two contributions: the decrease in the O-H bond energy due to the formation of the hydrogen-bonded adduct, δD_{OH} (> 0), and the bond dissociation energy of hydrogen bond formed, D_{HB} , as

$$\Delta H = \delta D_{\text{OH}} - D_{\text{HB}} \quad (3)$$

They thought that D_{HB} is an index better than ΔH for the strength of the hydrogen bond. Then a relationship between δD_{OH} and $\Delta\nu_{\text{OH}}$ is required to obtain the relationship between D_{HB} and $\Delta\nu_{\text{OH}}$. They approximated the stretching of the hydrogen-bonded OH by the anharmonicity stretching of free OH, and related δD_{OH} and $\Delta\nu_{\text{OH}}$ theoretically as follows:

$$\delta D_{\text{OH}} = (hcN/4\chi_e) \Delta\nu_{\text{OH}} = D_{\text{OHF}} (\Delta\nu_{\text{OH}}/\nu_e) = 0.131 \Delta\nu_{\text{OH}} \quad (4)$$

where h is Plank's constant, c is the speed of light, D_{OHF} is the bond dissociation energy of free O-H (= 420 kJ/mol), and ν_e is the wavenumber of harmonic vibration of the free OH in cm⁻¹, and χ_e is the anharmonicity constant for the oscillator.

Using eqs 3 and 4, eq 2 can be solved to obtain D_{HB} as follows:

$$D_{\text{HB}} = 0.198 \Delta\nu_{\text{OH}} + 2.64 [\text{kJ/mol}] \quad (5)$$

Now either eq 2 or eq 5 directly relates the OH wavenumber shift to the strength of hydrogen bonds for various phenol-base and alcohol-base hydrogen bonds in liquid phase.

New Method Developed for Estimating Strength Distribution of Hydrogen Bonds in Coal^{41,42}

Definitions and Basic Concepts of the New Method. We have attempted to develop a method to

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quantify the hydrogen bonds in coal based on the findings reviewed above. The hydrogen bond formation reaction of OH groups can be defined by the following equation:



where Coal-OH represents a hypothetical state in which the OH exists as a free OH group. The bases, B, in this case represent O and N in OH, COOH, C=O, and N-H groups.

We have decided to analyze the OH stretching absorption bands, because the information on the hydrogen bonds is concentrated on the absorption bands. To do so, several problems must be solved. How do we eliminate the effect of adsorbed water interacting with coal intimately? How do we determine the amount of each hydrogen bond from the complex absorption band? Are eqs 2 and 5 applicable to the hydrogen bond in coal? The water problem associated with KBr was overcome by using the DRIFT technique with neat coal samples.

The effect of adsorbed water was not intended to be eliminated but intended to be included in the analysis, since the adsorbed water affects significantly the hydrogen bonds in coal. Then the following hydrogen bond formation reaction was taken into account in addition to reaction 6.



where HO-H again represents a hypothetical state in which the OH exists as a free OH group. The bases, B', in this reaction involves O in water in addition to the bases in coal. This treatment looks apparently to make the analysis complicated, but in reality this facilitated the analysis as stated below.

The amounts of individual hydrogen bonds, in other words the amounts of OH contributing to different hydrogen bonds, were determined by the curve-resolving method. First, the absorption band ranging from 2400 to 3750 cm^{-1} was regarded to consist of the following 10 absorption bands: 7 OH stretch bands and 3 CH stretch bands.

- 3640 cm^{-1} ; free OH groups
- 3530 cm^{-1} ; OH- π hydrogen bonds
- 3400 cm^{-1} ; self-associated *n*-mers (*n* > 3)
- 3280 cm^{-1} ; OH-ether O hydrogen bonds
- 3150 cm^{-1} ; tightly bound cyclic OH tetramers
- 2940 cm^{-1} ; OH-N (acid/base structures)
- 2640 cm^{-1} ; COOH dimers
- 3050 cm^{-1} ; aromatic hydrogens
- 2993, 2920 cm^{-1} ; aliphatic hydrogens

The peak positions are a little different from those proposed by Painter et al.,²⁶ and the hydrogen bonds attributable to COOH dimers were also taken into account judging from the second derivative of the spectrum and the brain and eye examination. Figure 3 schematically shows the hydrogen bonds taken into account in this work. Assuming the Gaussian distribution for each absorption band, the spectrum was curve-resolved to obtain the intensity of each band. Of course, more complicated functions such as the Voigt function (mixture of Gaussian and Lorentzian functions) can be utilized for the curve resolving.²¹ However, we judged that the Gaussian distribution is precise enough for the curve resolving as was suggested by Solomon et al.²⁰

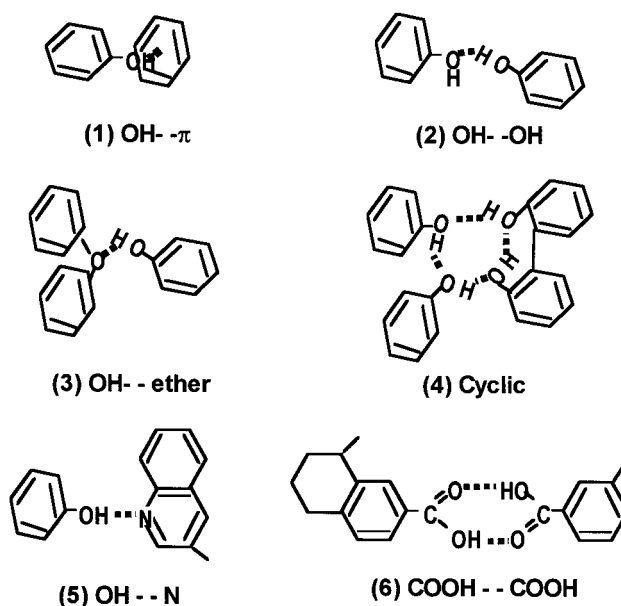


Figure 3. Schematic representation of hydrogen bonds assumed to exist in coal in this work.

Next, the absorptivity or the extinction coefficient of each band must be determined to convert the individual intensities to corresponding amounts of OH groups. It is known that the absorption intensity of OH stretch frequency forming a hydrogen bond increases with the increase of frequency shift, $\Delta\nu_{\text{OH}}$. Therefore, it is necessary to estimate the absorptivity of each absorption band independently in principle. Detoni et al. examined the change of absorptivity of the NH stretching band of isothiocyanic acid (HNCS) accompanying the formation of hydrogen bonds with various acceptors in CCl_4 systematically.⁴³ They found the following relationship between the absorptivity of the hydrogen-bonded NH, α_{NH} , and that of free NH, $\alpha_{\text{NH},0}$:

$$\alpha_{\text{NH}} = \alpha_{\text{NH},0}(1 + 0.0141 \Delta\nu_{\text{NH}}) \quad (8)$$

where $\Delta\nu_{\text{NH}}$ is the NH wavenumber shift. This relationship shows that the absorption intensity of the hydrogen-bonded NH increases in proportion to $\Delta\nu_{\text{NH}}$. On the basis of this work we arbitrarily assumed a similar relationship for the change in absorption intensity of hydrogen-bonded OH, and estimated the proportional constant from the intensity and the $\Delta\nu_{\text{OH}}$ values measured for several model compounds (benzoic acid and 2-naphthol) as

$$\alpha_{\text{OH}} = \alpha_{\text{OH},0}(1 + 0.0147 \Delta\nu_{\text{OH}}) \quad (9)$$

where α_{OH} is the absorptivity of the hydrogen-bonded OH and $\alpha_{\text{OH},0}$ is the absorptivity of the free OH. The proportionality constant obtained for the OH-associated hydrogen bonds (eq 9) was found to be very close to that for the NH-associated hydrogen bonds (eq 8). Thus we can calculate the amounts of OH contributing to different hydrogen bonds using eq 9 when we can estimate $\alpha_{\text{OH},0}$.

The last problem to be solved is whether eqs 2 and 5 are applicable to the hydrogen bond in coal. Their

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applicability is supported by the works of Larsen et al. (Figures 1 and 2). Figure 2 qualitatively shows that the OH shift increases with base strength as in the case for phenol–base hydrogen bonds, and Figure 1 suggests the equivalence of the $\Delta H (= q_{\text{st, specific}})$ values and $\Delta H_{\text{f, PFP}}$ values. These results suggest that the coal hydrogen bonds are treated in a similar way as the phenol–base hydrogen bonds. Although not directly related to the coal hydrogen bonds, Kiselev⁴⁴ found a linear relationship between the heat of adsorption, ΔQ_{a} , and the $\Delta\nu_{\text{OH}}$ for a hydroxylated silica surface and various vapors including steam. It was represented by

$$\Delta Q_{\text{a}} = 0.064 \Delta\nu_{\text{OH}} - 1.16 \text{ [kJ/mol]} \quad (10)$$

These works clarified that the OH wavenumber shift caused by the formation of hydrogen bonding is well related to the enthalpy change of the hydrogen bonding formation. Based on these considerations we have judged that eqs 2 and 5 are applicable to the hydrogen bond in coal as a first approximation. Using eqs 2 and 5, we can now estimate the strength of individual hydrogen bonds in coal from the $\Delta\nu_{\text{OH}}$ values.

Procedure To Estimate the Strength Distribution of Hydrogen Bonds. The procedure to obtain the strength distribution of hydrogen bonds by the proposed method is summarized as follows:

1. Divide the FTIR spectrum ranging from 2200 to 3700 cm^{-1} into 6 hydrogen-bonded OH bands, 3 CH stretch bands, and the free OH band, if it existed, by a curve fitting method as schematically given in Figure 4a. The Gaussian distribution was assumed for each absorption band in this work. Three CH stretch bands are easily eliminated from the spectrum. Since we employed in situ measurements, three CH stretch bands did not change during the measurement. It made it easy to strip off the CH bands from the OH bands.

2. Estimate the amount of OH for the j th peak, $(n_{\text{OH}})_j$, by the Beer law as follows:

$$(n_{\text{OH}})_j = (1/\alpha_j) A_j \quad (11)$$

where A_j and α_j are, respectively, the integral intensity and the absorptivity of the j th peak. In this analysis α_j was assumed to be represented by eq 9.

$$\alpha_j = \alpha_0 \{1 + 0.0147(\Delta\nu_{\text{OH}})_j\} \quad (12)$$

where α_0 is the absorption coefficient of the stretch vibration of the free OH. Then the amount of the OH corresponding to the j th peak, $(n_{\text{OH}})_j$, is given by

$$(n_{\text{OH}})_j = \frac{1}{\alpha_0 \{1 + 0.0147(\Delta\nu_{\text{OH}})_j\}} A_j \quad (13)$$

3. Calculate the strength of the j th hydrogen bond, $(-\Delta H)_j$ by eq 2 as

$$(-\Delta H)_j = 0.067 (\Delta\nu_{\text{OH}})_j + 2.64 \text{ [kJ/mol]} \quad (2)$$

The value of $(D_{\text{HB}})_j$ can also be obtained from eq 5 if necessary.

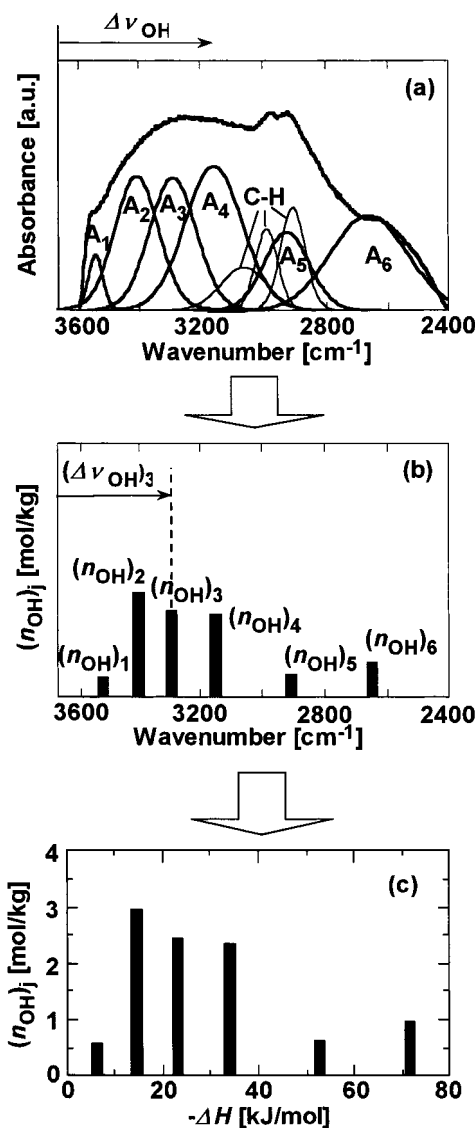


Figure 4. Procedure to obtain the strength distribution of hydrogen bonds by the proposed method.

4. $(n_{\text{OH}})_j$ vs $(-\Delta H)_j$ relationship gives the distribution of the strength of hydrogen bonds as shown schematically in Figure 4c.

Experimental Section

Samples. Seven Argonne premium coals and an Australian brown coal (Morwell) were used as coal samples. The ultimate analyses and the amount of OH and COOH oxygen^{45,46} are given in Table 1. Coal samples –200 mesh were further ground for 1 min in a mortar just before measurement. As model compounds for coal an ion-exchange resin (Mitsubishi Chemicals, WK11) that has carboxylic groups as ion-exchange sites (Figure 5) and a lignin (Nakalai Tesque, Co.) were also used. The amount of COOH in the resin was estimated to be 10.3 mol/kg by ¹³C NMR measurement.

Apparatus and Procedure. The diffuse reflectance spectrum at any sample, R , was measured at 4 cm^{-1} resolutions on a JEOL JIR-WINSPEC50 FTIR spectrometer with a microscope stage. A Mettler 84HPT hot stage, shown sche-

(45) Jung, B.; Stachel, S.; Calkins, W. H. Prepr. Pap—Am. Chem. Soc., Div. Fuel Chem. **1991**, 36 (3), 869–876.

(46) Schafer, H. N. S. *Functional Groups and Ion Exchange Properties*. In *The Science of Victorian Brown Coal*; Durie, R. A., Ed.; Butterworth: Heinemann, 1991; Chapter 7, p 334.

Table 1. Ultimate Analyses and Oxygen Distribution of 8 Coals Used [wt %]

coal (abbrev.)	ultimate analysis [daf]				oxygen content [daf]			
	C	H	N	O(diff.)	as COOH	as OH	as C=O	as ether
Morwell (MW)	67.1	4.8	0.7	27.4	7.97	5.92		
Beulah-Zap (ND)	72.9	4.8	1.2	20.1	3.81	9.16	1.96	2.28
Wyodak (WY)	75.0	5.4	1.1	21.0	3.33	7.68	0.74	2.56
Illinois #6 (IL)	77.7	5.0	1.4	13.5	0.23	5.86	0.93	0.57
Blind Canyon (UT)	80.7	5.8	1.4	13.5	0.23	5.22	0.63	3.68
Pittsburgh No. 8 (PITT)	83.2	5.3	1.6	8.8	0.16	4.32	0.18	2.08
Upper Freeport (UF)	85.5	4.7	1.6	7.5	0.14	1.96	0.44	0.36
Pocahontas (POC)	91.1	4.4	1.3	2.5	0.05	0.98	0.32	0.24

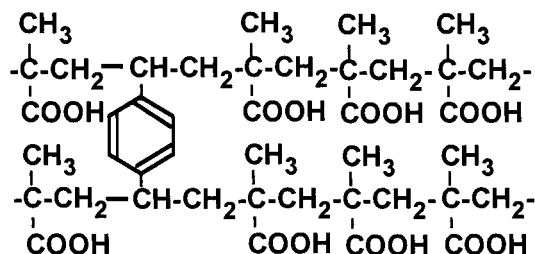


Figure 5. Structure of an ion-exchange resin used as a model compound for coal.

matically in Figure 6, was attached to the microscope stage for the in-situ measurement. About 0.5 mg of neat coal samples were leveled and pressed on the mirror by hand using a spatula. It is essential to make a flat surface for obtaining good and reproducible spectra. The coal samples were equilibrated at 30 °C in a flowing nitrogen stream. Then they were heated at the rate of 5 K/min up to 300 °C during which ultrahigh purity nitrogen was continually supplied at the rate of 100 cm³/min to prevent any possible leakage of air into the chamber and to keep the stability of the temperature. A BaF₂

disk was put on the pinhole from where the light passes through. The light source was a heated Ni–Cr wire and the detector was MCT (mercury cadmium telluride). The diffuse reflectance spectrum was collected by acquisition of 100 scans at 20 °C intervals. A mirror, which is believed not to absorb water, was used to obtain the background diffuse reflectance spectrum, R_0 . The ratio of R/R_0 was converted to the Kubelka–Munk (KM) function to obtain the spectrum corresponding to the absorbance. The spectrum thus obtained at any sample is simply called an FTIR spectrum in this paper.

Results and Discussion

Validity of in-Situ DRIFT Technique Employed.

As discussed above, there are several experimental problems to be solved for analyzing an FTIR spectrum quantitatively. However, most of the problems could be solved by using the in-situ DRIFT technique. The water adsorption problem was also overcome by analyzing the spectrum measured with the adsorbed water. Figure 7 shows the change of the FTIR spectra for the resin with

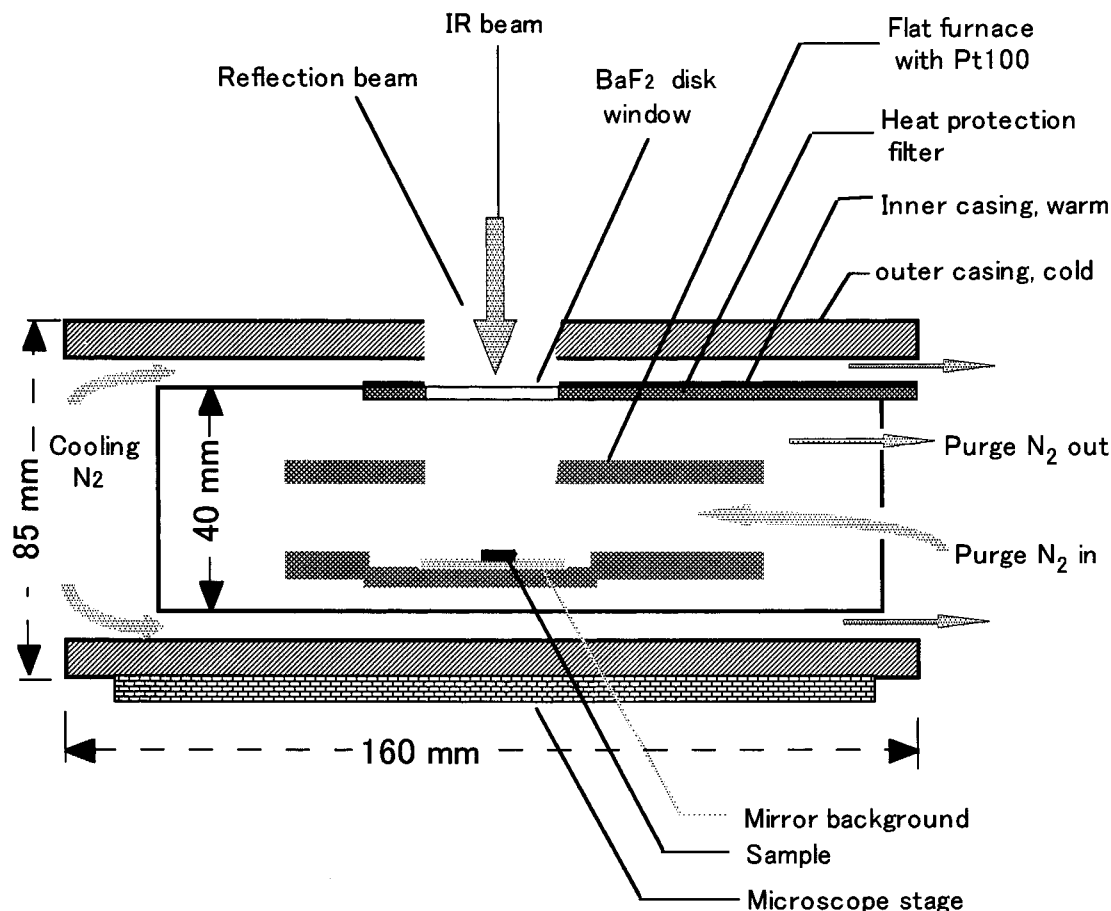


Figure 6. Schematic of a modified Mettler 84HPT hot stage used for in-situ FTIR measurements.

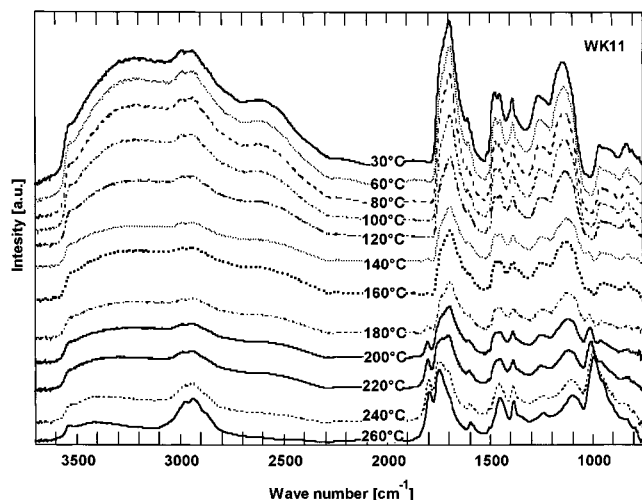


Figure 7. Change in the in-situ FTIR spectrum of the ion-exchange resin (WK11) with the increase of temperature.

the increase of temperature. One of the problems encountered by many investigators in using in-situ FTIR was the spectra quality at high temperatures due to the change in refractive index. Very beautiful spectra with almost flat baselines show that such a problem is well overcome by the DRIFT technique employed here. To examine the change of the OH absorption band region, the spectra ranging from 2400 to 3650 cm^{-1} were enlarged and shown in Figure 8. The weight change and the gas formation rates measured under the same experimental conditions using a TG-MS method are also shown in Figure 8 to clarify the change during the heat-up of the resin. When the resin was heated from room temperature to 140 $^{\circ}\text{C}$, the intensity of the absorption bands ranging from only 2800 to 3400 cm^{-1} decreased. This decrease can be well associated with the desorption of adsorbed water referring to the water formation profile in the lower figure. This also indicates that water is adsorbing with OH groups by rather weak hydrogen bonds. By further heating, all OH-associated absorption bands decrease significantly, and these decreases accompany again the formation of water as shown in the lower figure. The water formed in this temperature range is judged to come from the decomposition reactions of carboxylic groups represented by



This can be confirmed by the appearance of distinct absorption bands of an anhydride (-COOCO-) at near 1800 cm^{-1} as shown in Figure 7. Thus it was found that the changes of the OH absorption bands measured by the in-situ DRIFT technique give a lot of information, including the reaction of the early stage of pyrolysis. This will be shown more distinctively through the quantitative analysis made below.

Change of OH Absorption Bands of Coal with Heating. Figure 9 shows the in-situ FTIR spectra ranging from 2200 to 3700 cm^{-1} measured for the eight coals. Very beautiful and reproducible spectra could be obtained by use of the proposed measurement technique for all the coals. Very flat baselines were obtained at all the temperatures, and the spectra for POC did not change significantly above 70 $^{\circ}\text{C}$. This suggested that the spectra were not affected by the temperature below

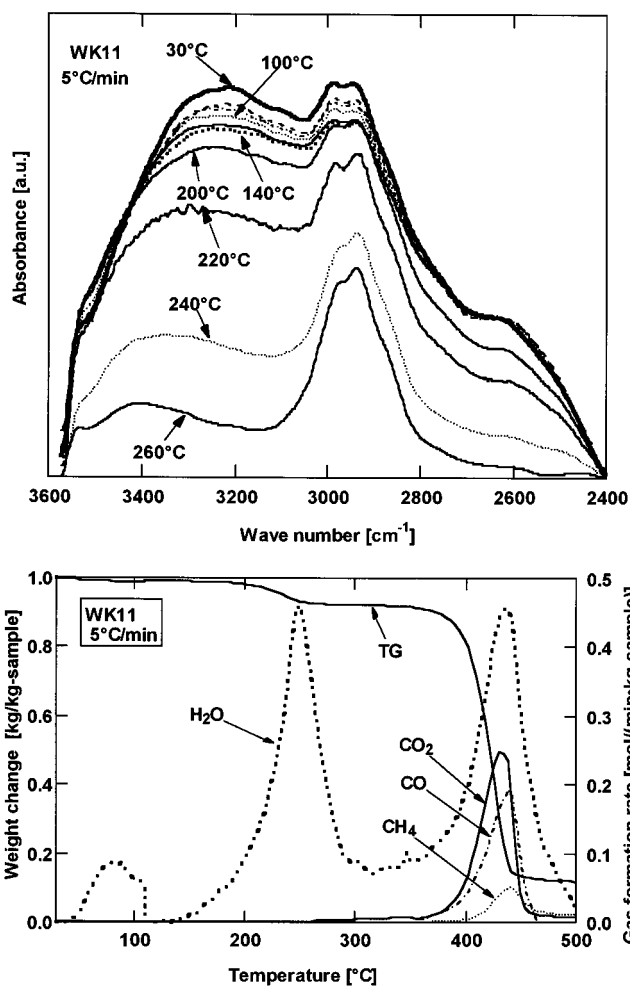


Figure 8. Changes in the OH stretching bands, weight, and gas formation rates during a heating of the ion-exchange resin (WK11).

300 $^{\circ}\text{C}$. Separate experiments were performed using kaolinite to check the change of spectra with increasing temperature up to 350 $^{\circ}\text{C}$. The mirror backgrounds at 30 $^{\circ}\text{C}$ and at corresponding temperatures were used, respectively, to get the FTIR spectra. The spectra did not change with the background at different temperatures. Then all the spectra shown in this work were obtained using the background at 30 $^{\circ}\text{C}$. This made the in-situ measurement convenient, fast, and reliable.

To get accurate information of hydrogen-bonded OH groups, it is essential to ensure that the artifact does not exist during experiments and/or during the data processing after experiments. It is easily checked by tracing the changes in the aliphatic and aromatic C-H bands. Because the C-H bond is hard to decompose or to form below 300 $^{\circ}\text{C}$, we can easily know whether some artifact exists or not from the variation of the 2890 and 2930 cm^{-1} bands (the absorption of aliphatic C-H bonds), and the 3050 cm^{-1} band (the absorption of aromatic C-H bond). It was found that these intensities were not affected by the temperature up to 300 $^{\circ}\text{C}$. Therefore, all the changes in the OH spectra were really what happened in coal during the heating. Now, significant changes in the OH spectra were judged to occur for MW, ND, and WY coals, whereas very little change was judged to occur for PITT and POC coals during the heating.

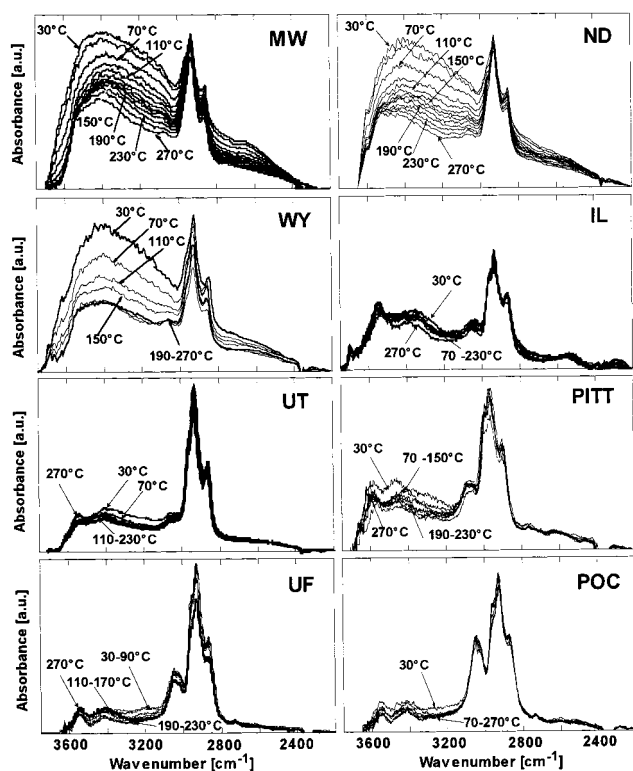


Figure 9. In-situ FTIR spectra measured at every 20 °C for seven Argonne premium coals and an Australian brown coal.

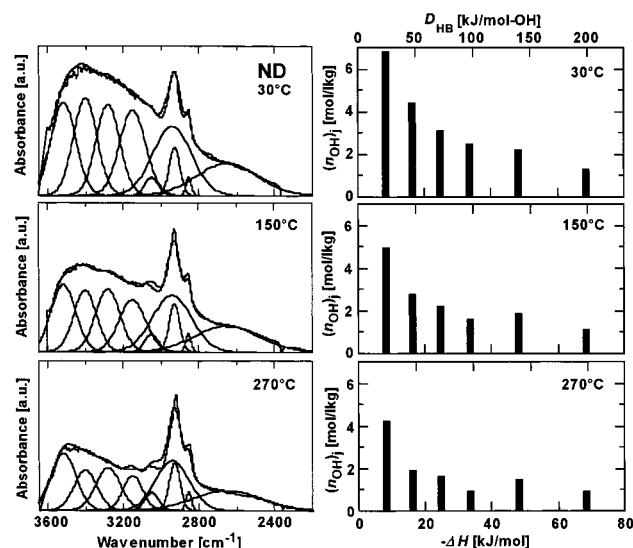


Figure 10. Six hydrogen-bonded OH stretching bands and three CH bands obtained by a curve resolving method and the strength distributions of hydrogen bonds estimated by the proposed method for ND coal.

Change in Strength Distribution of OH Associated with Hydrogen Bonds. All the spectra measured for the eight coals were analyzed by the procedure given above to estimate the change in HBD through the heating. Figure 10 shows the result of peak division and the HBD obtained for ND as an example. The spectra ranging from 2200 to 3650 cm^{-1} were divided into 9 peaks by a curve-fitting method. The six types of hydrogen bonds were abbreviated as follows: HB1: OH- π at 3530 cm^{-1} , HB2: OH-OH at 3400 cm^{-1} , HB3: OH-ether at 3280 cm^{-1} , HB4: cyclic OH-OH at 3150 cm^{-1} , HB5 at 2940 cm^{-1} ; OH-N, and HB6: COOH-COOH at 2650 cm^{-1} . These are in the order of

increasing strength. No free OH bands were detected for all the coals. In actual peak division, the peak positions were slightly changed, depending on the sample by referring to the second derivative of each spectrum. The bands for the C-H bonds did not change during the heating, then they were easily separated from the hydrogen-bonded bands. The amount of OH and the strength of each hydrogen bond, $(n_{\text{OH}})_j$, were calculated from each peak intensity, A_j , and the OH wavenumber shift, $\Delta\nu_{\text{OH}}$, with the aid of eq 13. To do so, the α_0 value must be estimated for each sample. If we assume that all adsorbed water is desorbed below 150 °C (the validity of this assumption is shown below), the total amount of OH (the sum of OH and COOH groups) given for each coal in Table 1 is equated to the total amount of OH at 150 °C. The total amount of OH, $(n_{\text{OH}})_{\text{total}}$, can be related to the intensity of each absorption band by

$$n_{\text{OH},\text{total}} = \sum_j (n_{\text{OH}})_j = \frac{1}{\alpha_0} \sum_j \left[\frac{1}{\{1 + 0.0147(\Delta\nu_{\text{OH}})_j\}} A_j \right] \quad (15)$$

By applying this relationship to the spectrum obtained at 150 °C α_0 value can be estimated for each coal sample. The strength distributions of hydrogen bonds thus estimated, $(n_{\text{OH}})_j$ vs $(-\Delta H)_j$ relationships, for ND are shown in the right figure in Figure 10. The strengths of individual hydrogen bonds represented by $-\Delta H$ values are HB1: 10 kJ/mol-OH, HB2: 17 kJ/mol-OH, HB3: 25 kJ/mol-OH, HB4: 35 kJ/mol-OH, HB5: 50 kJ/mol-OH, HB6: 70 kJ/mol-OH, and those represented by D_{HB} values are HB1: 24 kJ/mol-OH, HB2: 50 kJ/mol-OH, HB3: 74 kJ/mol-OH, HB4: 100 kJ/mol-OH, HB5: 141 kJ/mol-OH, HB6: 199 kJ/mol-OH. Since we assumed that all adsorbed water was desorbed by 150 °C, the distribution at 150 °C is the distribution of the coal dried and heated to 150 °C. The dried ND coal is rich in rather weak hydrogen bonds: 2.5 mol-OH/kg of HB1, 1.3 mol-OH/kg of HB2, and 1.1 mol-OH/kg of HB3. When the raw ND coal was heated from 30 °C to 150 °C, the amounts of weaker hydrogen bonds such as HB1, HB2, HB3, and HB4 decreased significantly. Since this decrease is due to the desorption of adsorbed water, it is found that water is interacting with coal hydroxyls by rather weak interactions. When the coal was further heated to 270 °C, all hydrogen bonds decreased. This decrease is judged to be due to the decomposition reactions of carboxylic groups such as eq 14. Thus it was clarified that the in-situ DRIFT technique and the analysis method proposed here are powerful to examine the change in hydrogen bonds in coal.

Sensitivity of FTIR to Adsorbed Water. In the course of various spectra measurements we have experienced how FTIR is sensitive to water. When a coal sample was heated to 130 °C to remove the adsorbed water and then cooled to 30 °C in an atmosphere of flowing dry nitrogen, the absorption bands ranging 3000 to 3500 cm^{-1} increased considerably. We have had difficulty in interpreting the unexpected change, and finally we found that it was the result of the adsorption of water from the "dry" nitrogen. The dried coal took up a fairly large amount of water very quickly even from the dry nitrogen containing water by less than 100 ppm.

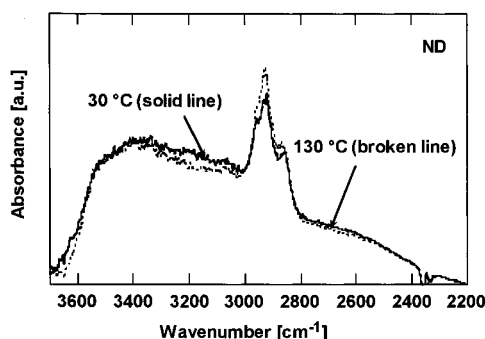


Figure 11. In-situ FTIR spectrum of ND coal heated to 130 °C and the spectrum of the coal cooled to 30 °C in an flowing ultrahigh purity nitrogen.

When we used an ultrahigh purity nitrogen containing water less than 10 ppm instead of the dry nitrogen as the carrier gas, very little change was observed between the spectrum at 130 °C and the spectrum of the coal cooled to 30 °C as typically shown for ND coal in Figure 11. The slight difference between the two spectra is probably due to rearrangement of hydrogen bonds upon cooling. Thus we found that in-situ measurements in a water-free atmosphere are indispensable for quantitative analysis of OH absorption bands. We were also impressed that the in-situ DRIFT technique would be a most sensitive method to analyze water in solid materials. These findings also suggested that the water problem cannot completely be removed when the conventional KBr pellet method was used.

Quantitative Analysis of Change in Hydrogen Bonds during the Heating. The changes of the amounts of the six hydrogen-bonded OH (HB1 to HB6) were estimated by the procedure presented above, then the changes of their amounts with increasing temperature are shown for the all eight coals in Figure 12. For lower rank coals, MW, ND, and WY, the amounts of weaker hydrogen bonds such as HB1, HB2, HB3, and HB4 decreased significantly below 150 °C. These decreases are associated with the desorption of adsorbed water as shown for the resin in Figure 8. With further increase of temperature, the total amount of hydrogen bonds, $(n_{\text{OH}})_{\text{total}}$, decreased for MW, ND, and WY, but it was kept almost constant for IL, PITT, UF, and POC. These results show that decomposition reactions of carboxylic groups start at around 200 °C for the lower rank coals which have many COOH groups as shown in Table 1. On the other hand, such reactions are negligible for the higher rank coals, because the COOH contents are very low for these coals. It is noteworthy that only the distribution changes without affecting the total amount of hydrogen bonds for UT, PITT, and UF above 200 °C. This means that the stronger hydrogen bond, HB5, shifted to weaker hydrogen bonds, HB1 and HB2 at higher temperatures. This phenomenon seems to be associated with the glass transition.

To examine the change in the hydrogen bonds in more quantitatively, total enthalpy for the formation of all OH associated hydrogen bonds, $(-\Delta H)_{\text{total}} (<0)$, at each temperature was calculated by

$$(-\Delta H)_{\text{total}} = \sum_j (n_{\text{OH}})_j (-\Delta H)_j \quad (16)$$

Utilizing $(-\Delta H)_{\text{total}}$ and the total amount of OH groups,

$(n_{\text{OH}})_{\text{total}}$, the average strength of hydrogen bonds, $(-\Delta H)_{\text{av}}$, can also be calculated by

$$(-\Delta H)_{\text{av}} = \frac{(-\Delta H)_{\text{total}}}{(n_{\text{OH}})_{\text{total}}} = \frac{\sum_j (n_{\text{OH}})_j (-\Delta H)_j}{\sum_j (n_{\text{OH}})_j} \quad (17)$$

Inserting eqs 2 and 13 into 17 gives

$$(-\Delta H)_{\text{av}} = \frac{\sum_j \left[\frac{1}{\{1 + 0.0147(\Delta\nu_{\text{OH}})_j\}} A_j \{0.067(\Delta\nu_{\text{OH}})_j + 2.64\} \right]}{\sum_j \left[\frac{1}{\{1 + 0.0147(\Delta\nu_{\text{OH}})_j\}} A_j \right]} \quad (18)$$

The $(-\Delta H)_{\text{total}}$ values are shown in Figure 12, and the $(-\Delta H)_{\text{av}}$ values for the temperatures higher than 150 °C are shown in Figure 13. The $(-\Delta H)_{\text{total}}$ value decreases with the increase of temperature due to the change in hydrogen bonds in coal. When the number of total OH groups, $(n_{\text{OH}})_{\text{total}}$, does not change, the decrease in $(-\Delta H)_{\text{total}}$ is due to the rearrangement of hydrogen bonds. When H₂O is produced during the heat treatment, the number of OH groups decreases by the two mechanisms, and consequently $(-\Delta H)_{\text{total}}$ decreases. The first mechanism is the desorption of adsorbed water and the other is the formation of H₂O by the decomposition of COOH groups. For MW, ND, and WY, both $(-\Delta H)_{\text{total}}$ and $(n_{\text{OH}})_{\text{total}}$ decreased with increasing temperature, indicating that the change in $(-\Delta H)_{\text{total}}$ is brought about by the formation of water. On the other hand, for UT, PITT, and UF, only the $(-\Delta H)_{\text{total}}$ value decreased without affecting the value of $(n_{\text{OH}})_{\text{total}}$ above 230 °C. This indicates that the rearrangement of hydrogen bonds occurred at above 230 °C as stated above. This rearrangement is well associated with the glass transition as detected by DSC by several investigators.^{20,21}

The changes in the average hydrogen bond strength, $(-\Delta H)_{\text{av}}$, in Figure 13 are also informative. The $(-\Delta H)_{\text{av}}$ values are around 20 to 24 kJ/mol-OH and kept almost constant during the heating for MW, ND, WY, IL, and UT. The $(-\Delta H)_{\text{av}}$ value for PITT is around 23 kJ/mol-OH below 230 °C, but it decreases to 20 kJ/mol-OH above 230 °C, indicating that the glass transition occurred between 230 and 270 °C. For high rank coals of UF and POC, the $(-\Delta H)_{\text{av}}$ values are 28 to 30 kJ/mol-OH, which are larger than those for the other coals by 4 to 8 kJ/mol-OH. The $(-\Delta H)_{\text{av}}$ value for UF also decreased to 23.7 kJ/mol-OH above 230 °C, again indicating the occurrence of the glass transition. The $(-\Delta H)_{\text{av}}$ values estimated here are rather close to the values reported as the strength of hydrogen bonding in the literature.^{1,2,17} A little bit larger $(-\Delta H)_{\text{av}}$ values for UF and POC are associated with the relative abundance of OH-N hydrogen bonds (HB5) in these coals. It was clearly shown that the glass transition behavior can be detected from the change in $(-\Delta H)_{\text{av}}$ value for higher rank coals. We can now estimate the change in enthalpies through the glass transition. They are, for example,

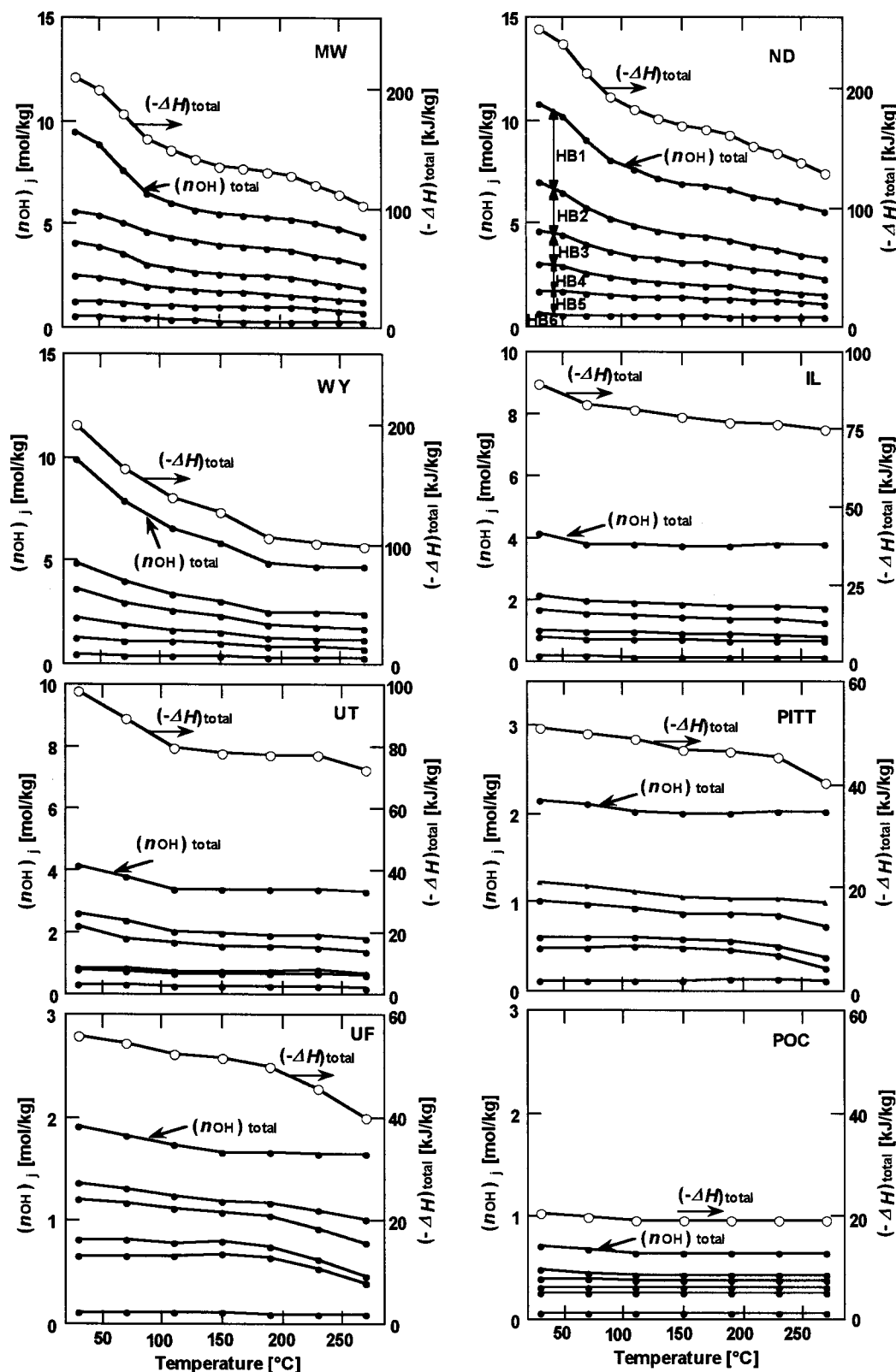


Figure 12. Change of $(nOH)_j$, $(nOH)_{total}$, and $(-\Delta H)_{total}$ with increasing temperature for the eight coals.

10 kJ/kg-coal and 7 kJ/mol-OH for UF, and 6 kJ/kg-coal and 3 kJ/mol-OH for PITT.

What we would like to stress here is that the value of α_0 is not required to calculate $(-\Delta H)_{av}$ as can be found from eq 18, which means that FTIR spectra measurements are self-sufficient to obtain $(-\Delta H)_{av}$. This is one of the merits of the proposed analysis method. This

facilitates the analysis, and therefore the accuracy of the $(-\Delta H)_{av}$ values is well expected.

Differentiation between Adsorbed Water and Decomposed Water. It has been rather difficult to distinguish the chemisorbed water and the water formed by decomposition reaction, which made it difficult to define the dried state of coal especially for lower rank

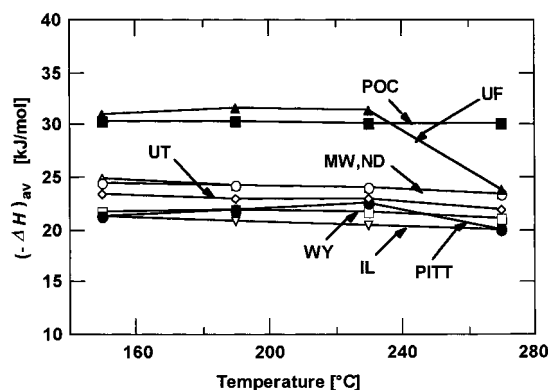


Figure 13. Change in the average strength of hydrogen bonds, $(-\Delta H)_{av}$, with increasing temperature for the eight coals.

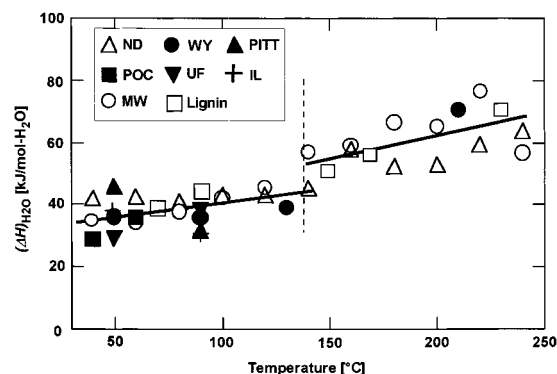


Figure 14. Changes in the water formation enthalpy, $(\Delta H)_{H_2O}$, with increasing temperature for the coals, the resin, and the lignin.

coals. We arbitrarily assumed above that all adsorbed water desorbs by 150 °C. Now we will examine the validity of the assumption.

In this analysis we could estimate the changes in the amount of OH, $(n_{OH})_{total}$, and the enthalpy related to hydrogen bonds, $(-\Delta H)_{total}$, as shown in Figure 12. Then we can estimate the change in the enthalpy related to hydrogen bonding with the formation of water by using the values of $(-\Delta H)_{total}$ and $(n_{OH})_{total}$ as

$$(\Delta H)_{H_2O} = 2 \frac{d(-\Delta H)_{total}}{d(n_{OH})_{total}} [\text{kJ/mol-H}_2\text{O}] \quad (19)$$

where 2 in the rhs was included to account for the fact that one H_2O molecule is involved in two hydrogen bonds. The magnitude of $(\Delta H)_{H_2O}$ thus estimated is well expected to be dependent of the mechanism of water formation. Then the $(\Delta H)_{H_2O}$ values calculated by eq 19 with the aid of eqs 2, 13, and 16 are shown against temperature in Figure 14. The values obtained for the resin and the lignin are also included in the figure for comparison. The $(\Delta H)_{H_2O}$ vs temperature relationships were so close to each other, and there was a distinct jump at about 140 °C: the $(\Delta H)_{H_2O}$ values below 140 °C were close to or slightly smaller than the heat of vaporization of water, ΔH_{vap} , whereas the $(\Delta H)_{H_2O}$ values above 140 °C were significantly larger than ΔH_{vap} . These results suggest that the water detected below 140 °C is the adsorbed water and that formed above 140 °C is the water formed by some decomposition reaction. Thus the HBD estimated by the proposed

method is found to be utilized to distinguish the type of water formed. We stress again that the value of α_0 or the value of $(n_{OH})_{total}$ is not required to obtain $(\Delta H)_{H_2O}$, as was the case to calculate $(-\Delta H)_{av}$. FTIR spectra measurements alone are enough to obtain $(\Delta H)_{H_2O}$.

Conclusion

A new method was presented to estimate the strength distribution of hydrogen bonds in coal, and its validity was examined by analyzing the change in the hydrogen bond distributions of 8 different coals, a resin, and a lignin during their heat treatment below 300 °C. The hydrogen bonds examined included the coal intramolecule hydrogen bonds and coal–water hydrogen bonds formed by hydroxyls in coal. The method analyzes the FTIR spectrum ranging from 2400 to 3700 cm^{-1} that are obtained using the in-situ diffuse reflectance IR Fourier transform (DRIFT) technique with neat, undiluted, coal samples.

The analysis method and the experimental technique employed clarified the following.

1. Water is taken up on coal even from a dry atmosphere so quickly that in-situ measurements in completely water-free atmosphere are indispensable for quantitative analysis of OH absorption bands. This suggested that the water problem cannot completely be removed when the conventional KBr pellet method was used.

2. Coal itself has hydrogen bonds ranging from 10 kJ/mol to 70 kJ/mol in strength. The relative abundance of the hydrogen bonds is highly dependent on coal type. Lower rank coals are rich in weaker hydrogen bonds associated with OH– π , OH–H, and OH–ether, whereas some high rank coals are rich in OH–N hydrogen bonds.

3. The average strength of hydrogen bonds was found to decrease above 230 °C for some bituminous coals without affecting the total number of hydrogen bonds. This clarified that the change accompanying the glass transition can be well traced by the proposed analysis method.

4. The enthalpy associated with the formation of water could be successfully estimated from solely the FTIR measurement. The enthalpy increased gradually up to 140 °C from 30 kJ/mol to 40 kJ/mol, but it increased in a stepwise manner to a level of 50 kJ/mol over 140 °C. This clarified that the water formation below 140 °C is due to the desorption of adsorbed water, and that the water formation above 140 °C is due to the decomposition reactions of COOH groups. This finding enabled us to define the dried state of coal definitely. It is also possible to examine quantitatively the early stage of pyrolysis of coal on the basis of this information.

Thus the validity and usefulness of the proposed method was clarified. We are sure that this method will be extended to analyze various solvent–coal interactions. The extension of this method to other fields may also be well expected.

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