

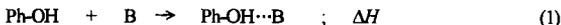
***In Situ* F.T.I.R. MEASUREMENT OF THE CHANGE IN HYDROGEN BONDING OF COAL THROUGH HEAT TREATMENT**

Kouichi Miura\*, Kazuhiro Mae, Li Wen, Takumi Kusakawa and Akiko Kumano  
Department of Chemical Engineering, Kyoto University, Kyoto 606-8501, Japan

**INTRODUCTION**

It is well known that hydrogen bonding plays an important role to keep the macromolecular structure of coal.<sup>1-5</sup> Several attempts have been made to estimate the amount and the strength of hydrogen bonding in coal. However, no definite methods have been presented for the estimation. One of the difficulties encountered for the estimation is the distribution of hydrogen bonding, and another problems associated with the estimation is the effect of adsorbed water. F.T.i.r. is believed to be a most powerful and convenient method to estimate the hydrogen bonding.<sup>6-11</sup> The water problem can not be completely overcome when the KBr pellet method was used, although the method is said to be suitable to quantitative studies.<sup>9</sup> Fuller and Smyrn<sup>10</sup> showed that the *in-situ* diffuse reflectance i.r. Fourier transform (DRIFT) technique with neat, undiluted, coal samples can be well utilized to trace the *in-situ* reactions such as oxidation, dehydration, etc. Painter *et al.*<sup>7</sup> clarified the attribution of hydrogen bonded absorption bands ranging from 2800 to 3600 cm<sup>-1</sup>. It is known that the absorption wave number of hydrogen bonded OH stretching vibration shifts from that of free OH by Δν<sub>OH</sub>, and that the Δν<sub>OH</sub> value increases with the increase of the strength of hydrogen bonding.

In liquid phase hydrogen-bonded adduct formation reactions between phenolic OH groups and various bases (B) have been examined in detail.<sup>12-15</sup>



where ΔH (< 0) is the enthalpy change of the reaction, and -ΔH is regarded as the strength of hydrogen bonding in general. Δν<sub>OH</sub> (>0) for this reaction is the wave number difference between the free OH in Ph-OH and the hydrogen bonded OH in Ph-OH⋯B. Through separate measurements of ΔH [kJ/mol] and Δν<sub>OH</sub> [cm<sup>-1</sup>] for many phenol-base combinations a linear relationship was found to hold between them by many investigators. The relationship obtained by Drago *et al.*<sup>13</sup>, for example, is given by

$$-\Delta H = 0.067\Delta\nu_{\text{OH}} + 2.64 \quad (2)$$

For solid-gas interactions, Kiselev<sup>16</sup> found that a linear relationship between the heat of adsorption, ΔQ<sub>a</sub> [kJ/mol], and the Δν<sub>OH</sub> [cm<sup>-1</sup>] for a hydroxylated silica surface and various vapors including steam. It was represented by

$$\Delta Q_a = 0.064\Delta\nu_{\text{OH}} - 1.16 \quad (3)$$

These works clarified that the OH wave number shift caused by the formation of hydrogen bonding is well related to the enthalpy change of the hydrogen bonding formation. However, neither the distribution nor the amount of hydrogen bonding were not taken into account in these works.

Recently Miura and his co-workers<sup>17</sup> have presented a method to estimate the strength distribution of hydrogen bonding (HBD) in coal by use of F.T.i.r. and DSC. The method was developed by combining and extending the works of Drago *et al.*, Painter *et al.*, and Kiselev. They found the following -ΔH vs. Δν<sub>OH</sub> relationship for water free coals:

$$-\Delta H = 0.069\Delta\nu_{\text{OH}} \quad (4)$$

In their analysis, however, F.T.i.r. measurements were performed using the KBr pellet technique, and hence the water effect might not be completely eliminated. Furthermore, the absorption coefficients for different hydrogen bonded OH were assumed to be same as the first approximation. The latter assumption affects the amount of hydrogen bonding but does not affect the -ΔH vs. Δν<sub>OH</sub> relationship given by eq 4.

To overcome these weak points in the former analysis, an *in-situ* diffuse reflectance F.T.i.r. (DRIFT) technique was employed for the measurement of spectra, and the change in absorption coefficients was taken into account in this paper. The improved method was applied to estimate the change of hydrogen bonding during the heating of the Argonne premium coals from 30 to 290 °C.

**ANALYSIS METHOD**

The method to obtain the HBD was originally presented in a previous work.<sup>17</sup> The method was improved in this paper by taking into account the change in absorption coefficients for different hydrogen bonded OH groups. The procedure to obtain the HBD by the improved method is summarized as follows:

1. Divide F.T.i.r. spectrum ranging from 2200 to 3700 cm<sup>-1</sup> into several hydrogen bonded peaks by a curve fitting method as schematically given in Fig. 1(a). The Gaussian distribution was assumed for each absorption band in this work. Three peaks associated with aromatic and aliphatic CH stretch vibrations are easily eliminated from the spectrum.
2. Estimate the amount of OH for the j-th peak, (n<sub>OH</sub>)<sub>j</sub>, by the Beer law as follows:

$$(n_{\text{OH}})_j = \alpha_j A_j \quad (5)$$

where A<sub>j</sub> and α<sub>j</sub> are respectively the integral intensity and the absorption coefficient of the j-th peak. In this analysis α<sub>j</sub> was assumed to be represented by the equation presented by Detoni *et al.*<sup>18</sup> for the hydrogen bonded NH groups

$$\alpha_j = \frac{\alpha_0}{1 + 0.0141(\Delta\nu_{\text{OH}})_j} \quad (6)$$

where  $\alpha_0$  is the absorption coefficient of the stretch vibration of the free OH. Then the amount of the OH corresponding to the  $j$ -th peak,  $(n_{OH})_j$ , is given by

$$(n_{OH})_j = \frac{\alpha_0}{1 + 0.014(\Delta \nu_{OH})_j} A_j \quad (7)$$

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

$$(-\Delta H)_j = 0.069 (\Delta \nu_{OH})_j \quad (8)$$

4.  $(n_{OH})_j$  vs.  $(-\Delta H)_j$  relationship gives the distribution of the strength of hydrogen bonding as shown schematically in Fig. 1(c).

**Table 1. Ultimate analyses and oxygen distribution of 8 Argonne premium coals used [wt%]**

Coal (abbrev.)	Ultimate analysis [d.a.f.]				Oxygen content [d.a.f.]			
	C	H	N	O(diff)	as COOH	as OH	as C=O	as Ether
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
Lewinston-Stockton (ST)	82.6	5.3	1.6	9.8	0.20	2.70	0.18	2.67
Pittsburg#8 (PITT)	83.2	5.3	1.6	8.8	0.16	4.32	0.18	2.08
UpperFreeport (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

## EXPERIMENTAL

**Coals samples.** Eight Argonne premium coals were used as samples. The ultimate analyses and the amount of OH and COOH oxygen<sup>19</sup> are given in Table 1. Coal samples -200 mesh were further ground for 1 minute in a mortar just before measurement.

**Apparatus and procedure.** All the IR spectra were measured at 4  $\text{cm}^{-1}$  resolution on a JEOL JIR-WINSPEC50 F.T.i.r. spectrometer with a microscope stage. A Mettler 84HPT hot stage, shown schematically in Fig. 2, was attached to the microscope stage for the *in-situ* measurement. A mirror, which is believed not to absorb water, was used as a background. 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 nitrogen was continually supplied at the rate of 100  $\text{cc}/\text{min}$  to prevent any possible leakage of air into the chamber and to keep the stability of the temperature. A BaF<sub>2</sub> disc was put on the pin hole from where the light passes through. The light source was a heated Ni-Cr wire and the detector was MCT (mercury cadmium-tellurium). F.T.i.r. spectrum was collected by acquisition of 100 scans at every 20 °C of interval.

## RESULTS AND DISCUSSION

**Change of spectra with heating.** Figure 3 shows the *in-situ* F.T.i.r. spectra ranging from 2200 to 3650  $\text{cm}^{-1}$  for four coals measured at every 20 °C. One of the problems encountered by many investigators in using *in-situ* F.T.i.r. was the spectra quality at high temperatures due to change in refractive index. Very beautiful and reproducible spectra could be obtained by use of the proposed measurement technique for all the coals in this work. Very flat base lines were obtained at all the temperatures, and the spectra for POC were almost same above 70 °C. This suggested that the spectra were not affected by the heating. Separate experiments were performed using kaolinite to check the change of spectra with increasing temperature up to 350 °C. The mirror backgrounds at 30 °C and at corresponding temperatures were used respectively to get the F.T.i.r. spectra. The spectra do not change with the background at different temperatures. Then all the spectra shown in this work were obtained using the background at 30 °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 change in the aliphatic and aromatic C-H bands. Because the C-H bond is hard to decompose or to form below 300 °C, we can easily know whether some artifact exists or not from the variation of the 2890 and 2930  $\text{cm}^{-1}$  bands (the absorption of aliphatic C-H bond), and 3050  $\text{cm}^{-1}$  band (the absorption of aromatic C-H bond). It was found that these intensities were not affected by the temperature up to 300 °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 ND and WY coals, whereas very little change was judged to occur for PITT and POC coals during the heating for the four coals given in Fig. 2.

**Change in strength distribution of OH associated with hydrogen bondings.** 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 4 shows the result of peak division and the HBD distributions obtained for ND as an example. The spectra ranging from 2200 to 3650  $\text{cm}^{-1}$  were divided into 9 peaks by a curve-fitting method. The peak assignments were determined as follows by referring to the work of Painter *et al.*<sup>7</sup>: six hydrogen bonded bands (HB1 at 3516  $\text{cm}^{-1}$ ; OH- $\pi$ , HB2 at 3400  $\text{cm}^{-1}$ ; OH-OH, HB3 at 3280  $\text{cm}^{-1}$ ; OH-ether, HB4 at 3150  $\text{cm}^{-1}$ ; cyclic OH-OH, HB5 at 2940  $\text{cm}^{-1}$ ; OH-N, and HB6 at 2650  $\text{cm}^{-1}$ ; COOH-COOH) and three C-H bands (3050, 2993, and 2920  $\text{cm}^{-1}$ ). No free OH band was 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 bonding were calculated from each peak intensity,  $A_j$ , and the OH wavenumber shift,  $\Delta\nu_{OH}$ , with the aid of eqs 7 and 8, where the total OH value given in Table 1 was used as the value at 150 °C to estimate  $\alpha_0$  in eq 7. The strength distributions of hydrogen bonding thus estimated,  $(n_{OH})_j$ , vs.  $(-\Delta H)_j$  relationships, for ND are shown in the right of Fig. 4. It is clearly shown that the amount of weakly hydrogen bonded OH preferentially decreases with the increase of temperature.

**Quantitative analysis of change in hydrogen bonding during the heating.** The changes of the amounts of the six hydrogen bonded OH with increasing temperature are shown for four coals in Fig. 5. As is expected from the spectra shown in Fig. 4, the amounts of HB1 to HB4 decrease significantly with increasing temperature for ND and WY, whereas all the hydrogen bondings do not change with increasing temperature for POC. The decrease in the total amount of OH with increasing temperature is related to the formation of  $H_2O$ . It is noteworthy that only the distribution changes without affecting the total amount of OH for PITT above 230 °C. This means that stronger hydrogen bonding, HB5, shifted to weaker hydrogen bondings, HB1 and HB2, above 230 °C.

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

$$(-\Delta H)_{total} = \sum_j (n_{OH})_j (-\Delta H)_j \quad [\text{kJ/kg}] \quad (9)$$

Utilizing  $(-\Delta H)_{total}$  and the total amount of OH groups,  $(n_{OH})_{total}$ , the average strength of hydrogen bonding,  $(-\Delta H)_{av}$ , can also be calculated by

$$(-\Delta H)_{av} = \frac{(-\Delta H)_{total}}{(n_{OH})_{total}} = \frac{\sum_j (n_{OH})_j (-\Delta H)_j}{\sum_j (n_{OH})_j} \quad (10)$$

The  $(-\Delta H)_{total}$  values and the  $(-\Delta H)_{av}$  values are shown in Fig. 5 and Fig. 6, respectively.  $(-\Delta H)_{total}$  decreases with the increase of temperature due to the changes in the hydrogen bondings. When the number of total OH groups does not change, the decrease in  $(-\Delta H)_{total}$  is due to the rearrangement of hydrogen bondings. When  $H_2O$  is produced during the heat treatment, the number of OH groups decreases by the two mechanisms, and consequently  $(-\Delta H)_{total}$  decreases. The first mechanism is the desorption of adsorbed water and the other is the formation of  $H_2O$  by the decomposition of two OH groups. For ND and WY, both  $(-\Delta H)_{total}$  and  $(n_{OH})_{total}$  decreased with increasing temperature, indicating that the change in  $(-\Delta H)_{total}$  is brought about by the formation of water. On the other hand, for PITT above 230 °C, only the  $(-\Delta H)_{total}$  value decreased without affecting the value of  $(n_{OH})_{total}$ . This indicates that the rearrangement of hydrogen bondings occurred at above 230 °C as stated above. This rearrangement may be associated with the glass transition as detected by DSC by several investigators.<sup>20,21</sup>

The changes in the average hydrogen bonding strength,  $(-\Delta H)_{av}$ , in Fig. 6 are also informative. The  $(-\Delta H)_{av}$  values are around 20 to 24 kJ/mol-OH and kept almost constant during the heating for ND, WY, UT and IL. The  $(-\Delta H)_{av}$  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 to 270 °C. For high rank coals of UF and POC, the  $(-\Delta H)_{av}$  values are 28 to 30 kJ/mol-OH, which are larger than for the other coals by 4 to 8 kJ/mol-OH. The  $(-\Delta H)_{av}$  value for UF also decreased to 23.7 kJ/mol-OH above 230 °C, again indicating the occurrence of the glass transition. The  $(-\Delta H)_{av}$  values estimated here are rather close to the values reported as the strength of hydrogen bonding in the literature.<sup>1-3</sup> A little bit larger  $(-\Delta H)_{av}$  values for UF and POC are associated with the relative abundance of OH-N hydrogen bonding in these coals. It was clearly shown that the glass transition behavior can be detected from the change in  $(-\Delta H)_{av}$  value for higher rank coals.

What we would like to stress here is that the value of  $\alpha_0$  is not required to calculate  $(-\Delta H)_{av}$ , as can be found from eqs 7, 8, and 10, which means that only F.T.i.r. spectra measurements are enough to obtain  $(-\Delta H)_{av}$ . This is a great merit of the proposed analysis method. Then the accuracy of the  $(-\Delta H)_{av}$  values are 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. In this analysis we could estimate the changes in the amount of OH,  $(n_{OH})_{total}$ , and the enthalpy related to hydrogen bonding,  $(-\Delta H)_{total}$ , as shown in Fig. 5. 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

$$(\Delta H)_{H_2O} = 2 \frac{d(-\Delta H)_{total}}{d(n_{OH})_{total}} \quad [\text{kJ/mol-H}_2\text{O}] \quad (11)$$

where 2 in the r.h.s. was included to account for the fact that one  $H_2O$  molecule contains two OH groups. The magnitude of  $(\Delta H)_{H_2O}$  thus estimated is well expected to be dependent on the mechanism of water

formation. Then the  $(\Delta H)_{\text{H}_2\text{O}}$  values calculated by eq 11 with the aid of eqs. 7, 8, and 9 are shown against temperature in Fig. 7. The values obtained for an Australian brown coal (Morwell; MW) and a lignin are also included in the figure for comparison. The  $(\Delta H)_{\text{H}_2\text{O}}$  vs. temperature relationships were so close each other, and there was a distinct jump at about 140 °C: the  $(\Delta H)_{\text{H}_2\text{O}}$  values below 140 °C were close to or slightly smaller than the heat of vaporization of water,  $\Delta H_{\text{vap}}$ , whereas the  $(\Delta H)_{\text{H}_2\text{O}}$  values above 140 °C were significantly larger than  $\Delta H_{\text{vap}}$ . These results suggest that the water detected below 140 °C is the chemisorbed 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. Finally we would like to stress that the value of  $\alpha_0$  or the value of  $(n_{\text{OH}})_{\text{total}}$  is not required to obtain  $(\Delta H)_{\text{H}_2\text{O}}$  as was the case to calculate  $(-\Delta H)_{\text{H}_2\text{O}}$ . Only F.T.i.r. spectra measurements are enough to obtain  $(\Delta H)_{\text{H}_2\text{O}}$ . This is a great merit of the proposed method and it simplifies the procedure to obtain  $(\Delta H)_{\text{H}_2\text{O}}$ .

## CONCLUSION

*In situ* F.T.i.r. measurements were performed for the Argonne premium coals to estimate the change in hydrogen bonding through heat treatment. Neat, undiluted, coal samples were placed in a specially designed cell and they were heated from room temperature up to 300 °C in an inert atmosphere. F.T.i.r. spectra were collected in every 20 °C using the diffuse reflectance infrared Fourier transform (DRIFT) technique and the spectra ranging from 2200 to 3650  $\text{cm}^{-1}$  were divided into 6 hydrogen bonded OH peaks and other peaks. The strength distribution of hydrogen bonding (HBD) at each temperature was well estimated through the analysis of the divided peaks by the proposed method. By utilizing the HBD the changes in enthalpies associated with the desorption of water, the glass transition, and the decomposition of OH groups were well estimated. Only F.T.i.r. 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* F.T.i.r. measurement method and the analysis method for obtaining HBD was well clarified.

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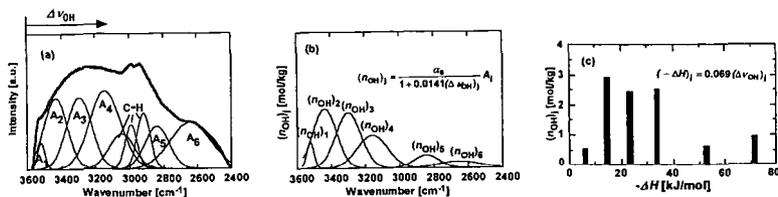


Figure 1 Procedure to obtain HBD from the spectra ranging from 2200 to 3650  $\text{cm}^{-1}$ .

