NON-MAGIC ANGLE SPINNING NMR - AN APPROACH TO DETERMINE THE CHEMICAL SHIFT TENSORS IN CHAR PARTICLES

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INTRODUCTION

Carbon-13 NMR spectroscopy has been widely accepted as a major analytical technique for studying fossil fuels. Axelson[1] and Davidson[2] have reviewed the various solid state NMR spectroscopic techniques for coal studies. Cross polarization/magic angle spinning (CP/MAS)[3] provides information on aromaticity while the dipolar dephasing technique (DD/MAS)[4] provides additional definition of the structure of coal by using the ^{13}C-^{1}H dipolar coupling to separate the carbons into sub-classes; i.e., those that are strongly coupled to protons from those that are weakly coupled in both the aliphatic and aromatic regions of the spectrum. The combination of these two experimental procedures permits one to derive a carbon skeletal structure of coal samples.[5,6]

MAS experiments produce narrow lines in solids but valuable structural information is lost; i.e., the chemical shift anisotropy (CSA) which is a manifestation of the three-dimensional shielding of the nucleus by the surrounding electrons.[7] The CSA is a second rank tensor having three principal elements σ_{11}, σ_{22}, and σ_{33} characterized by unique resonance frequencies. These three tensor components taken together with the isotropic shielding value (the MAS value which is the average of the three tensor components) provide valuable data regarding the local electronic environment. The tensor can be obtained from the ^{13}C NMR spectrum of a finely powdered sample and the tensor elements are extracted by analysis of the line shape. This technique provides not only tensor components but population values as well. However, the spectral analysis is complicated if more than one tensor is present and unique results are not always achievable. Evenso, Pines, et al.[8] used the technique to analyze the static spectra of several coals. These workers succeeded in differentiating the contributions from aromatic and condensed aromatic carbons. Furthermore, they pointed out that there is little difference in the isotropic chemical shifts between these types of carbons and these shift differences cannot be resolved in a CP/MAS experiment. The DD/MAS experiment has been shown to differentiate between benzene-like (i.e., C-H) and non-protonated aromatic carbons[5] (substituted plus inner, or bridgehead) but the resolution of substituted and inner carbons is not readily attainable with standard MAS experiments. The shielding anisotropies of the three general types of aromatic carbons are quite different and, in principal, should be resolvable in the "non-spinning" experiment.

Only for isolated carbons, or for simple compounds where break-points in the powder pattern are discernible, is it possible to obtain unique fits of the line shape. Tensor information can be extracted by other techniques such as analysis of the spinning side bands from slow spinning MAS experiments[9] and variable angle sample spinning[10-13] (VASS). In this study we have used the static and VASS methods to study pertinent model compounds and have used these data as a guide to analyze line shapes and extract CSA tensor values and population factors in coals. The experimental techniques are applicable to chars as well as coals. The data permit us to estimate the size of the polycondensed aromatic structure that is the main structural component in chars. The aromatic structure of coal chars should provide valuable information regarding their reactivity.

EXPERIMENTAL

1. NMR Spectroscopy

The NMR spectra were obtained on a Bruker CXP-100 as described previously.[6] The VASS method has been described by Sethi, et al.[13]

2. Spectral Fitting Procedure

The NMR powder pattern analyses were carried out by means of recently developed fitting methods[14]. The technique is briefly described as follows. It is assummed that spins are only experiencing orientation dependent chemical shift interactions. This is usually the case when employing high power proton decoupling. Single spectral simulation requires an initial estimate of these parameters: 1) the principal values of the different CSA's or a linear combination of elements in an irreducible form; 2) the relative intensities; and 3) a broadening factor. One or more of these parameters can be locked to some predetermined or known value, which is then held constant throughout the fitting process. For example, in model organic compounds, the relative intensity is usually locked to the atomic ratios given by the molecular structure. In coals, however, these population parameters are allowed to vary freely so as to provide quantitative data on individual carbon types. Theoretical spectra are calculated using the "POWDER" method[14]. The parameters are adjusted with a simplex optimization routine to minimize the sum of squares deviation between the theoretical and experimental spectra. In cases which necessitate obtaining spinning spectra at different angles, all spectra are fit simultaneously with the same set of CSA values. The total sum of squares from all spectra is used as the minimization criteria. Using this technique, the redundant data provide refinements in fitting parameters which, for a single spectrum, may exhibit ill-conditioned behavior.

RESULTS AND DISCUSSION

Aromatic CSA bands can be calssified into four different sub-groups which have tensor components that exhibit variations of ca. 10-20%. These groups are: 1) benzene-like (sp^2 C-H); 2) substituted (e.g. alkylated); 3) condensed (inner and bridgehead); 4) carbons

bonded to heteroatoms (nitrogen, oxygen, etc.).[15] The spectrum of an isolated carbon in a static sample presents a characteristic powder pattern which exhibits break points corresponding to the tensor elements of the individual carbons of each sub-class. Examples of the isotropic peak superimposed with their first three sub-classes, together with their isotropic peaks, are given in Figure 1. These three sub-classes represent the predominant types of aromatic carbons present in chars and high rank coals. An unambiguous tensor analysis usually cannot be performed on static lineshapes due to the overlap of several different CSA bands. This problem is especially accute for aromatic carbons since the upfield components of these bands are usually buried under the much narrower aliphatic resonances. The static spectrum of 1,2,3,6,7,8-hexahydropyrene provides a convenient representation of this problem. In addition, this molecule contains the types of carbons of interest in chars and high rank coals. The components of the individual aromatic carbon tensors have been simulated together with their composite pattern. This composite pattern is compared with the experimental data (Figure 2). The low field components are resolved but the high field (σ_{33} components) are obscured by the aliphatic carbons.

The VASS method scales the individual carbon tensors with respect to their isotropic frequencies by a factor of $1/2(\cos 3\theta^2-1)$ where θ is the spinning angle relative to the external magnetic field.[13] The break points from different bands change as θ is changed. The high field component of the aromatic carbon shielding tensors can be inverted through the isotropic value by proper selection of θ. Hence, overlapping tensor components can be unscrambled by this technique. In addition, a change in θ produces pronounced changes in all of the aromatic tensors so that the line shape is no longer a scaled replica of the static powder pattern. Such intensity and shape changes are readily recognized in our fitting routines which are sensitive to small changes in the line shape. In Figure 3, one observes the line shape changes of an alkylated aromatic carbon as the spinning angle is changed. In Figure 4 the VASS data on hexahydropyrene has been simulated and the tensor components are given in Table 1.

The ability to fit experimental data with high precision is vital to the analysis of complex materials. The hexahydropyrene model is of sufficient complexity to demonstrate the feasibility of unscrambling overlapping tensor components. The availability of multiple angle data decreases the chance of encountering a given spectrum which is insensitive to one or more of the adjustable parameters and therefore reduces ill-conditioned fits of the data.

Using the fitting procedure described above, we have fit the anthracite data (Figure 5). With an aromaticity value $f_a = 1.0$, no alkylated carbons are present and, hence, a multiple angle fit of the data was not deemed necessary. A two tensor fit of the static spectrum produced the results presented in Table 1. The population factor of 0.13 for the C-H tensor is essentially the same as the atomic ratio H/C = 0.123 for this coal. Hence, we are able to independently verify that the method gives valid results.

The anthracite provides a useful model for a char that has been subjected to extensive pyrolysis or to a high temperature environment and thus may be thought of as one extrema of a char model. On the other hand, coals that undergo pyrolysis for relatively short periods of time or at moderate temperatures are not composed entirely of polycondensed aromatic rings. Aromaticity values in the range 0.8 - 1.0 are observed in chars.[16] The inertinite macerals semi-fusinite and fusinite found in coals provide a useful model for char. Natural processes of heat and pressure have produced a char-like material. Such is the case for the Aldwarke Silkstone inertinite (86% inertinite) consisting chiefly of charcoal-like fusinite with an f_a value of 0.88.[6] The tensor components (see Figure 6) and population factors contained in Table 1 provide a distribution of the three major types of aromatic carbons present and one is not required to calculate the atomic ratio for hypothetical unsubstituted nuclei (H_{aru}/C_{ar}) as has been done in the past.[16] One can now directly measure this parameter together with the fraction of substituted carbons without resorting to calculated approximations.

The experimental value of H_{aru}/C_{ar} = 0.39 has been reported previously by means of dipolar dephasing data[6] and, hence, this value was used in fitting the spectra. The fit of the VASS data provided the other two tensors. The population of inner carbons (0.54) and substituted carbons (0.07) provide the remainder of the aromatic structural types. The substituted carbon population is of the order of 0.10, or less, and the total aliphatic carbon content is 0.12. Using the elemental analysis, i.e., the H/C ratio, it is clear that the alkyl substituents, on average, consist of 1-2 carbon fragments and that the non-methyl carbons are highly substituted.

The VASS technique provides a very useful means for supplementing other types of NMR data and is particularly useful in assessing the structure of polycondensed aromatic materials such as chars. As char reactivity is an important consideration in combustion studies, NMR data may be able to play a significant role in structure/reactivity correlation.

ACKNOWLEDGMENTS

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TABLE 1

Tensor Components[a] for Aromatic Carbons

Sample/Carbon Type	σ_{11}	σ_{22}	σ_{33}	Population[b] Factor
1,2,3,6,7,8 hexahydropyrene				
Benzene-like	225	128	22	0.40
Substituted	231	168	9	0.40
Inner	203	197	-6	0.20
Anthracite (PSOC-867)				
Benzene-like	217	137	20	0.13
Inner	194	180	-8	0.87
Inertinite[c]				
Benzene-like	223	149	17	0.39
Substituted	231	161	46	0.07
Inner	204	192	-30	0.54

a. ppm from TMS.

b. Based on total aromatic carbon present.

c. Semi-fusinite from Aldwarke Silkstone coal (Great Britain). The sample is described in reference 6.

FIGURE CAPTIONS

FIGURE 1. Chemical shielding tensors of aromatic carbons. The characteristic shapes are used to fit overlapping tensor elements. The narrow isotropic line obtained by magic angle spinning is also shown for purposes of clarity.

FIGURE 2. The static spectrum (top) of 1,2,3,6,7,8 hexahydropyrene. The individual tensors for the three different types of carbons are shown (bottom) together with the composite pattern. This theoretical fit of the data is superimposed in the top of the figure. Only the simulated aromatic carbon tensors are shown.

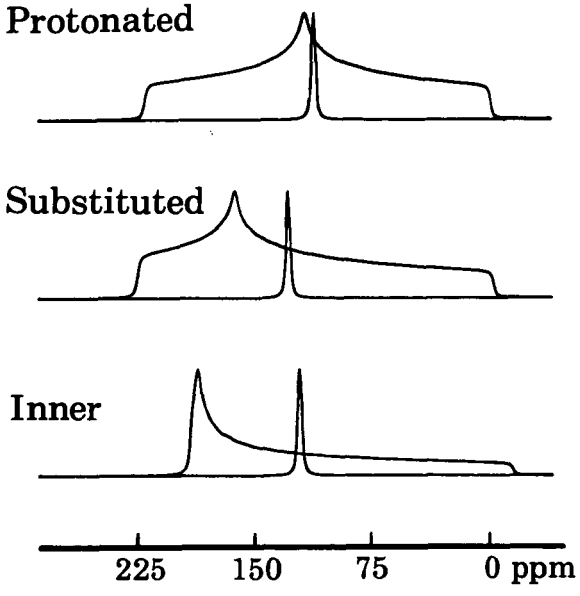
FIGURE 3. The tensor for a substituted aromatic carbon is simulated as a function of θ, the spinning axis relative to the magnetic field. The VASS experiment can be used to scale the position of the tensor components σ_{11}, σ_{22}, and σ_{33}. At the magic angle, $\theta = 54.7°$, the components converge to the isotropic value.

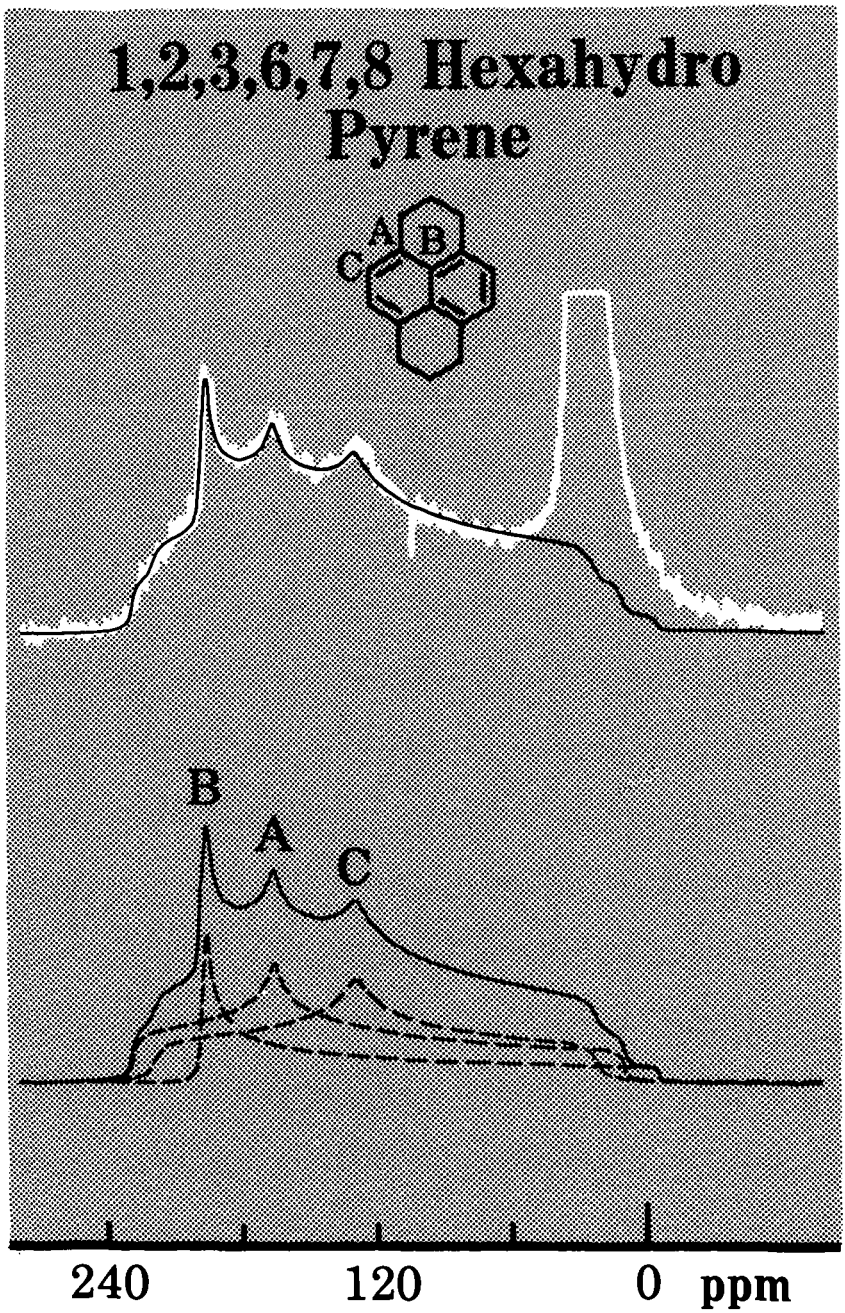
FIGURE 4. VASS spectra of 1,2,3,6,7,8 hexahydropyrene together with the simulated spectra arising from the aromatic carbons.

FIGURE 5. Experimental and simulated spectra of an anthracite coal. The two tensor fit gives near ideal correlation and the population factor for the benzene like tensor is within experimental error of the H/C value.

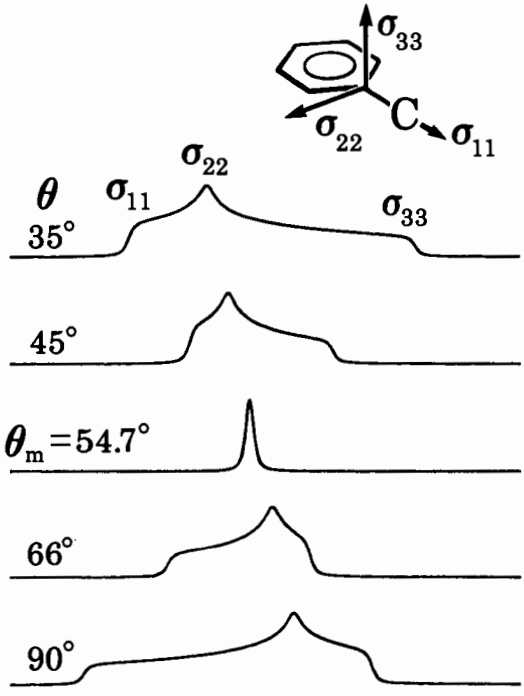
FIGURE 6. VASS spectra of Aldwarke Silkstone inertinite maceral (fusinite). The simulated spectrum of the aromatic carbons (bottom) is used to portray the population factors. The simulated aromatic carbon spectra at 43° and 72° are overlaid on the experimental data.

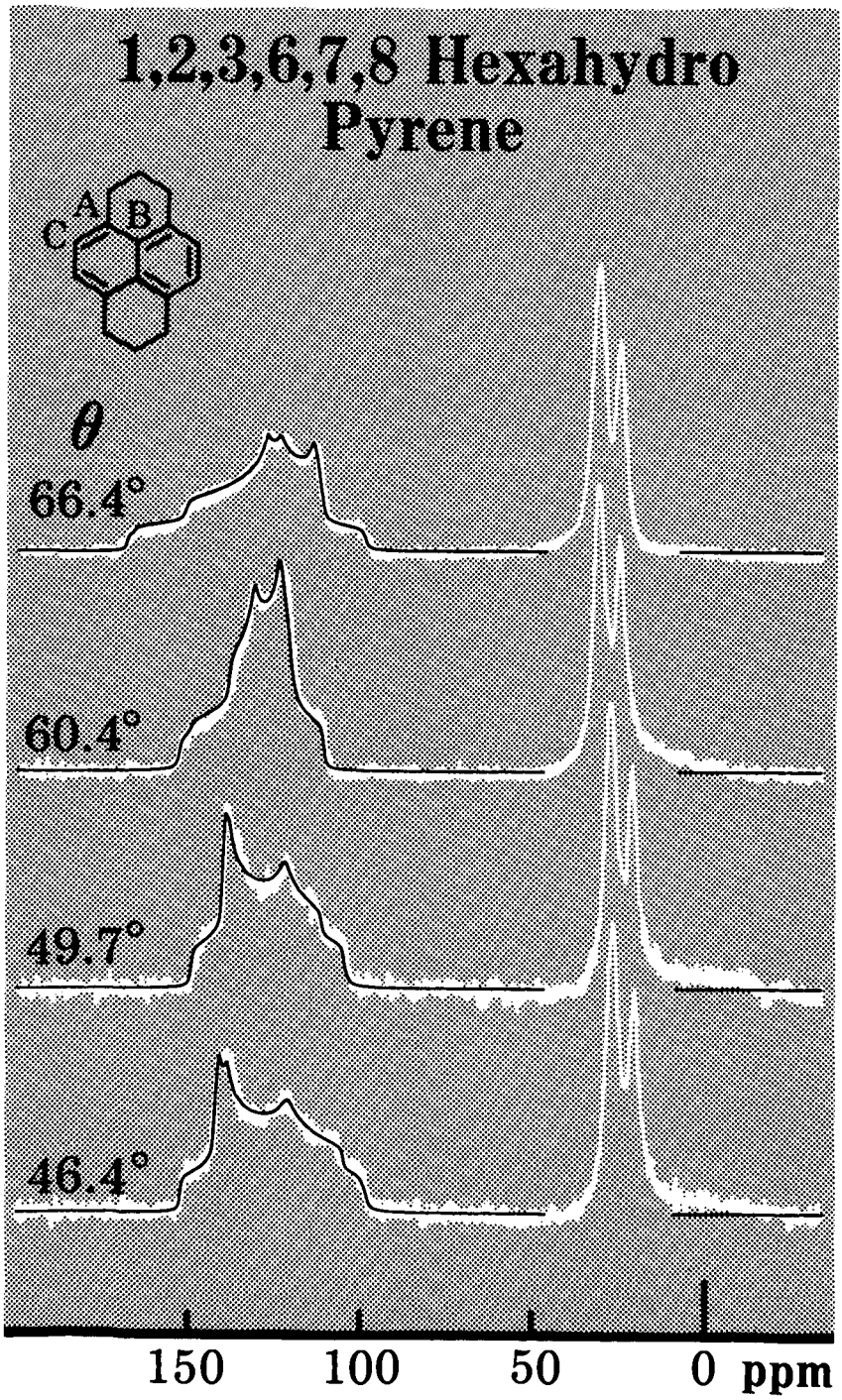
CSA
(aromatic carbons)

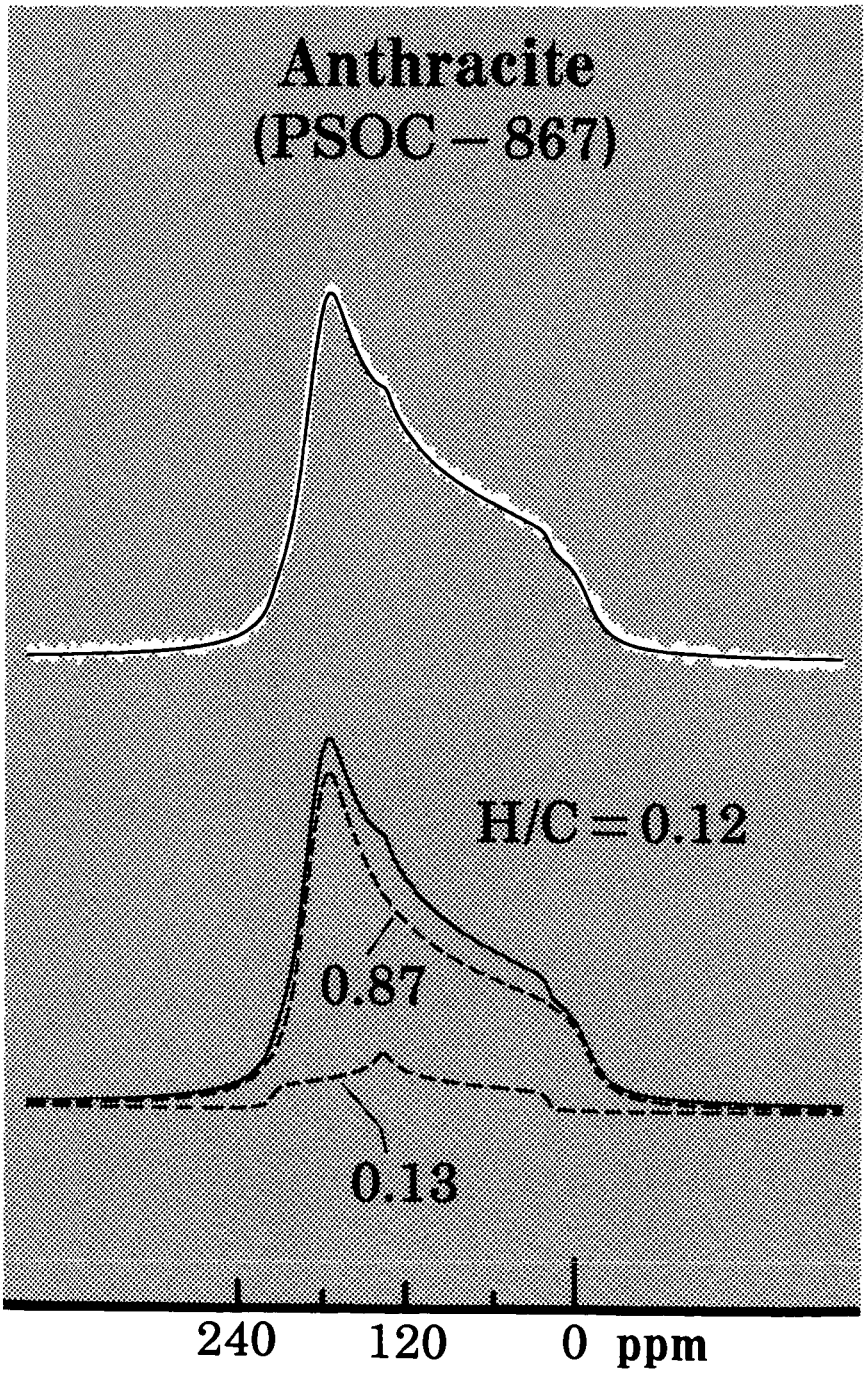


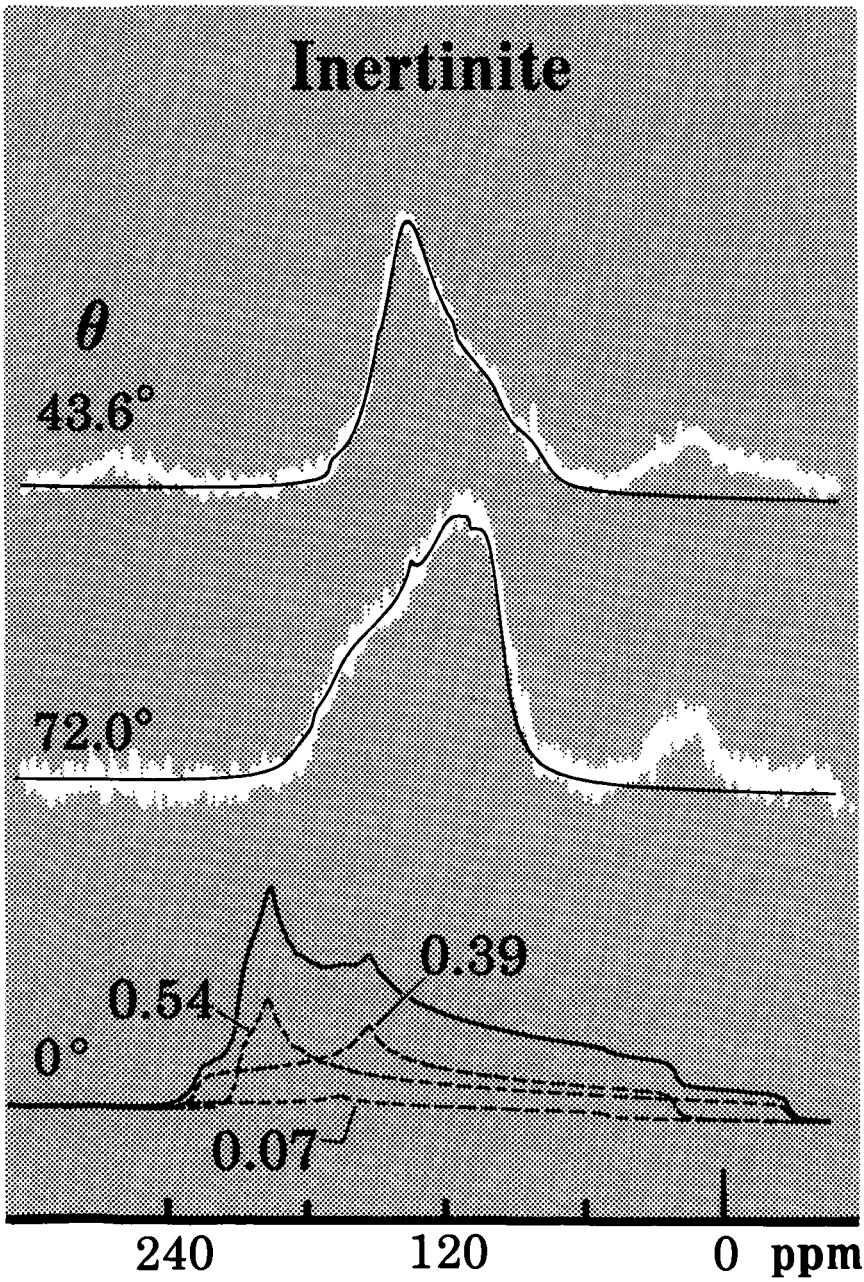

1,2,3,6,7,8 Hexahydro
Pyrene
A
B
C
B
A
C
240
120
0 ppm

VASS




1,2,3,6,7,8 Hexahydro Pyrene
A
B
C
θ
66.4°
60.4°
49.7°
46.4°
150
100
50
0 ppm


Anthracite
(PSOC – 867)
H/C = 0.12
0.87
0.13
240
120
0 ppm


Inertinite
θ
43.6°
72.0°
0°
0.54
0.39
0.07
240
120
0
ppm