USE OF INTRA- AND INTER-MOLECULAR MODELS TO SIMULATE THE WIDE ANGLE X-RAY SCATTERING OF COALS.

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INTRODUCTION. Hirsch et al.,[1] using the terminology of diffraction where $d = \lambda/2 \times \sin\theta$ for first order reflections in the x-ray experiments, assigned this peak to the average distance between layers which were proposed to contain the poly-cyclic units at the molecular level in coals. Using copper K_α Xrays, they found this peak (quite broad) to occur at $2\theta \approx 25°$, corresponding to $<d> \approx$ 3.5 Å. Their proposal of layering, at the molecular level in coals, has been verified, both by molecular modeling[2] and x-ray analysis using more modern equipment and several of the Argonne Premium Coals,[3] but their use of ideal diffraction concepts to define structuring in coals is troubling because coals are not crystalline.

An alternative method for relating the measured x-ray intensities, which now may be accurately obtained using modern quantum counting equipment and computer-controlled data acquisition and processing method, has been utilized by our group.[4,5] This method correlates the measured intensity, which is a series of broad maxima and minima, with the average short-range structural unit in the coal and has been illustrated in the scattering studies of liquids, solutions, and amorphous solids. The Debye relationship correlates the structure of any molecular-level species, averaged of time and space, with the simulated wide angle phase interference curve caused by that species by:
$$j(q) = (\textstyle\sum\sum q \times r_{ab})^{-1} \times \textstyle\sum\sum n_{ab} \times \sin(q \times r_{ab});$$
where n_{ab} is the number of a-b atom pairs which occur at the distance r_{ab} in the structure, $f_a(q)$ and $f_b(q)$ are the scattering powers of atoms a and b, respectively, and $q = [4 \times \pi/\lambda] \times \sin\theta$.[6] For several of the Argonne Premium Coals, the average intra-molecular structural unit, (i.e., the average PC and its attachments) have been reasonably well identified;[7,8] so the n_{ab}'s and the r_{ab}'s for the average intra-molecular structural unit may be determined using three-dimensional geometry and then used to calculate the simulated phase interference curve for that coal using the Debye equation. This has been accomplished for several coals.[4]

The actual phase interference curve, $i(q)$, may be obtained from the wide angle x-ray scattering (WAXRS) experiment. The comparison of $j(q)$ to $i(q)$ allows a judgement in the validity of the structural model used to calculate $j(q)$, i.e., the array of n_{ab}'s and the r_{ab}'s that define that model. The comparison may be quantified by:
$$\tau^2 = \textstyle\sum\{i(q) - j(q)\}^2/\textstyle\sum i(q)^2.$$
The lower the value of τ, the better the agreement between the experimentally measured phase interference curve and the phase interference curve calculated from the model.

Solum et al propose that the average poly-cyclic unit in Pittsburgh #8 (PIT) coal is *ca.* C_{15} with four attachments.[7] Shown in Figure 1 is the simulated phase interference curve calculated for the C_{15} unit. Also shown in Figure 1 are the experimentally measured $i(q)$'s using both Mo K_α and Cu K_α Xrays.[3] As previously noted, the agreement between the experimentally determined $i(q)$ and the $j(q)$ calculated from the intra-molecular model based on C_{15} agree well at $q > 3$ Å^{-1}. The $j(q)$ curve calculated from the C_{15} structural model is featureless in from 1.0 - 3.0 Å^{-1}; but the experimentally measured $i(q)$ has a large maximum, centered at ca. 1.6 Å^{-1} with minima preceding and following this maximum. Similar results have been obtained for other coals.[3,4] Thus, it may be concluded that the dominant maximum in the measured x-ray intensity curves for coals, located at *ca.* 1.7 -1.9 Å^{-1}, is not due to structuring within the average PC unit.

Recently, an improved explanation of the measured x-ray intensities, expanding on the layering concept, has been proposed as the result of an x-ray scattering study of Beulah Zap lignite.[9] This procedure incorporates the concept of molecular-level layering in coals by calculating the distances between atoms in adjacent layers within the average short-range structural domain for that coal and correlating these distances with the structure curve calculated for each coal from wide angle x-ray scattering (WAXRS) experiments.

The objective of this study is to simulate the dominant peak in each experimentally determined $i(q)$ using simplified structural models which approximate the average PC unit in the coal as a disc whose radius may be estimated from the NMR information available in the literature.

RESULTS. Shown in Figure 2 are several crude models of layering in the short-range domains in coals. The models differ, of course, in the number of layers in the average domain. To relate each of the models to coals, it has been assumed that the radius of the average PC unit (rad) is ca. 2.5 Å and average distance between the layers (<d>) is *ca.* 3.8 Å which is similar to the average inter-layer distance reported for a number of the Argonne Premium Coals.[3] Shown in Figure 3 are the relative frequencies of the atom-pair distances (i.e., the structure curve) calculated from each model by:

$$F(r) = \sum \{rad^2 + [n \times <d>]^2\}^{1/2};$$

where n describes the relationships between the layers in the model, and r is the distance between the atom in the various layers.

Using the Debye eq., each frequency function has been transformed into reciprocal space to produce its corresponding j(q). The simulated phase interference curve for each layer model is presented in Figure 4. Although the inter-layer structural models differ in the number of layers contained within each, their resulting phase interference curves are similar; with each featuring a maximum in the $q = 1.8$ Å^{-1} region. Minima precede and follow this maximum. The sharpness of the maximum is related to the number of layers in the short-range structural domain.

In the three layer model, C–C atom-pair distances are expected to be centered at *ca.* 4.5 Å and at *ca.* 8.0 Å with a relative peak intensity of 2/1. The j(q) calculated for the three layer model is similar to the experimentally determined i(q) obtained for PIT. Shown in Figure 5 is the j(q) calculated from the three layer model compared to the i(q) measured for Pittsburgh #8 coal. For this comparison, $\tau = 0.021$ when <d> = 3.92 Å and rad = 2.6 Å. This very low structure correlation factor verifies the excellent agreement between i(q) and the J(q) calculated from the 3-layer model. The average interlayer distance determined by this method is similar to the average interlayer spacing distance reported by the earlier non-ideal diffraction interpretation of the secondary x-ray intensity reported for PIT.

The inter-molecular structure curve has been obtained by Fourier transform of the inter-molecular portion of the experimentally determined phase interference curve for PIT. This inter-molecular structure curve contains two maxima with relative intensities of 2/1. In Figure 6, this inter-molecular structure curve is compared to the atom-distance/frequency function calculated for the three layer model. The good agreement between these two functions indicates that the average short-range structural domain in PIT contains three layer units.

CONCLUSIONS. A simplified inter-layer model of the layering of the PC units in coals is consistent with both the phase interference curve obtained for Pittsburgh #8 coal by wide angle x-ray scattering a This model also predicts an atom-pair frequency curve which is consistent with the inter-molecular structure curve obtained for PIT.

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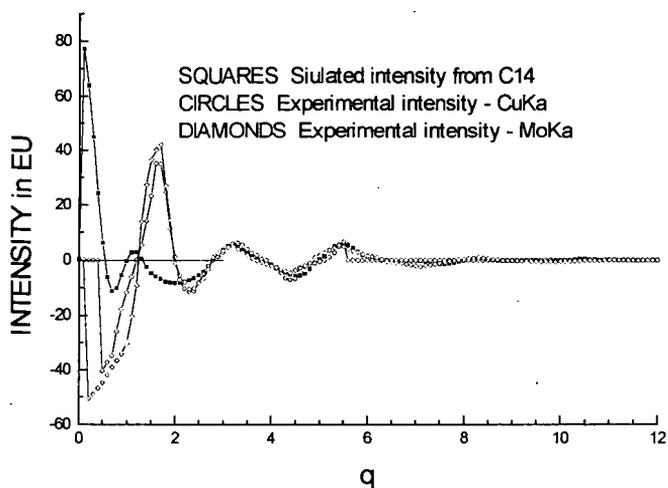
Figure 1. Comparison of the experimental phase interference curves for PIT with the simulated phase interference calculated for the C_{15} poly-cyclic unit.
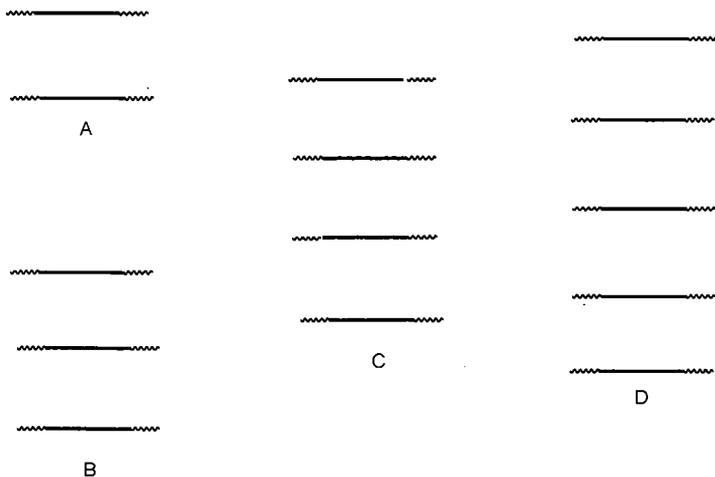
Figure 2. Models of molecular-level layering. Two layers (A), three layers (B), four layers (C), and five layers (D).
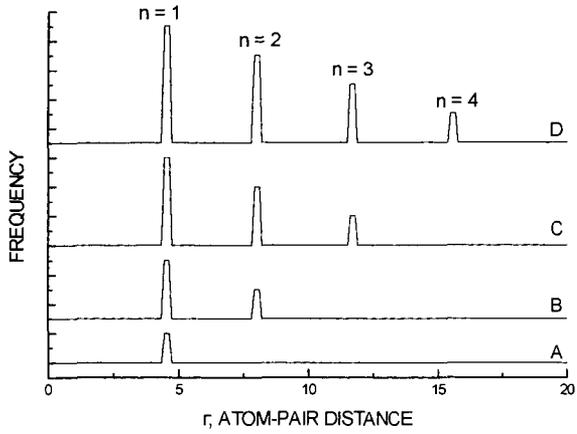
Figure 3. Frequency vs. atom-pair distance for the two-layer model (A), three-layer model (B), four-layer model (C), and the five-layer model (D).
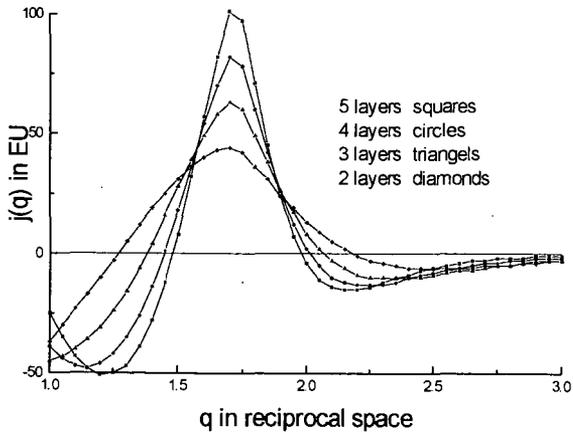
Figure 4. Simulated phase interference curves for the four inter-layer models.
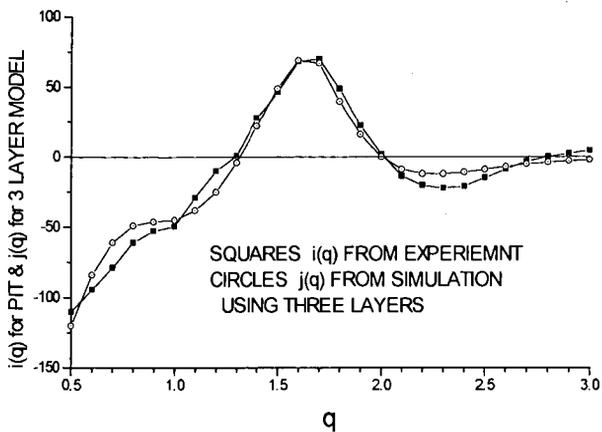
Figure 5. The i(q) for PIT compared to the optimized j(q) for the three-layer model.
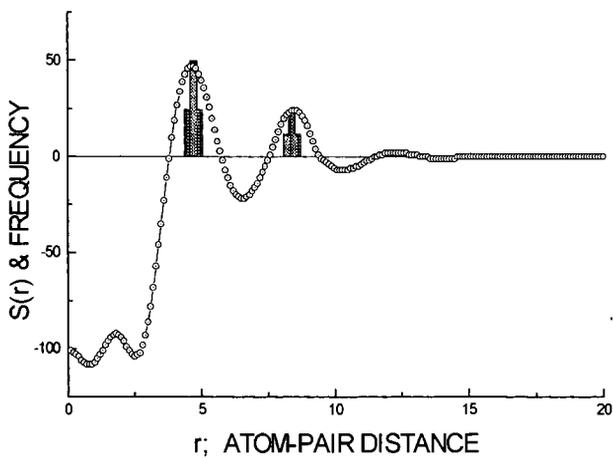
Figure 6. Inter-molecular structure curve for PIT compared to the frequency vs. atom-pair distance graph for the three-layer model.

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