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Advanced NMR-Based Techniques for Pore Structure Analysis of Coal

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Background

One of the main problems in coal utilization is the inability to properly characterize its complex pore structure. Coals typically have micro/ultra-micro pores but they also exhibit meso and macroporosity. Conventional pore size techniques (adsorption/condensation, mercury porosimetry) are limited because of this broad pore size range, microporosity, reactive nature of coal, samples must be completely dried, and network/percolation effects. Small angle scattering is limited because it probes both open and closed pores. Although one would not expect any single technique to provide a satisfactory description of a coal's structure, it is apparent that better techniques are necessary. We believe that measurement of the NMR parameters of various gas phase and adsorbed phase NMR active probes can provide the resolution to this problem. We will investigate the dependence of the common NMR parameters such as chemical shifts and relaxation times of several different nuclei and compounds on the pore structure of model microporous solids, carbons, and coals. In particular, we will study the interaction between several small molecules (^{129}Xe, ^{3}He, $^{2}H_2$, $^{14}N_2$, $^{14}NH_3$, $^{15}N_2$, $^{13}CH_4$, $^{13}CO_2$) and the pore surfaces in coals. These molecules have been selected for their chemical and physical properties. A special NMR probe will be constructed which will allow the concurrent measurement of NMR properties and adsorption uptake at a variety of temperatures. All samples will be subjected to a suite of "conventional" pore structure analyses. These include nitrogen adsorption at 77 K with BET analysis, CO_2 and CH_4 adsorption at 273 K with D-R (Dubinin-Radushkevich) analysis, helium pycnometry, and small angle X-ray scattering as well as gas diffusion measurements. The project combines expertise at the UNM (pore structure, NMR), Los Alamos National Laboratory (NMR), and Air Products (porous materials).

Work completed during the last quarter

We now have two suites of well-characterized microporous materials including oxides (zeolites and silica gel) and activated carbons from our industrial partner, Air Products in Allentown, PA. Our current work may be divided into three areas: small-angle X-ray scattering (SAXS), adsorption, and NMR.

1. SAXS.

Since the last report, we have made the required changes in the vapor adsorption apparatus for adsorbing the contrast match agent onto the sample. We added a constant temperature bath to vary the temperature of the dibromomethane liquid to change the vapor pressure. The porous solid sample is immersed in a water bath to minimize temperature fluctuations. This way we can accurately obtain various values of P/P_o. We found that running the adsorbed samples for longer times gave us better statistics. We also found that the optimum time for loading the sample at the desired vapor pressure was 24 hours.

First, unloaded and liquid loaded samples of CPG-75 were run to assess the degree of contrast matching. CPG-75 is a phase-separated porous glass with a nominal pore diameter of 7.5 nm. The characteristic SAXS intensity curve of the CPG disappeared when the sample was fully loaded except at small Q values (large feature size) as shown in Figure 1. This means that the sample was fully contrast matched. The small variation in intensity at small Q for the liquid loaded samples could be the result of density variations in the sample or surface roughness on the outside of the samples. The contrast matching for the various values of P/P_o (which showed relative loading) of dibromomethane on CPG-75 showed a nice trend. As the relative loading increased, the porod part of the scattering curve moved more to the left. This is as expected because as the relative loading increases, more and more dibromomethane gets adsorbed. The structure should become smoother and the porod part of the curve should become steeper. This will shift the curve so that it flattens at smaller q values (see Figure 2). Therefore for higher loading, we find longer flattened portions. We find that the peak at Q equal to $0.03Å^{-1}$ does not show much change till a P/P_o value of 0.78. This is consistent with the theory for pore filling where we got a P/P_o value of 0.75 using the Kelvin Equation. The position of the peak is indicative of the scattering length of the sample. The fact that the peak position does not change may mean that the layer of adsorbed dibromomethane is very thin. This is probably true. At P/P_o of 0.78, volume filling must be occurring and the structure changes. It becomes smoother and hence the peak disappears. We see a sharp fall in transmission at loading of 0.78 and above. The loaded sample also scatters very little. These observations must indicate that volume filling must be occurring at P/P_o of 0.78 or around that value. The contrast matching experiments do show a nice trend. However we find that at higher loading the statistics of the curve are poor and we have to run the sample on the SAXS for very long time periods. The analysis is in progress so that we can quantify the changes in the curve with respect to the change in pore structure.

2. Adsorption.

In the previous quarter, high pressure gas sorption studies were carried out on a series of activated carbons supplied by Air Products. Methane sorption was carried out at room temperature and carbon dioxide sorption was carried out at 0 degrees C. During this quarter, it was decided to extend sorption studies to the low-pressure range, i.e., in the range 0-1 atm. All low-pressure studies were carried out using automated low-pressure sorption systems; carbon dioxide and methane sorption was performed on a Micromeritics ASAP 2000 with a micropore analysis software, and nitrogen adsorption was carried out on a Quantachrome Autosorb-1. The low-

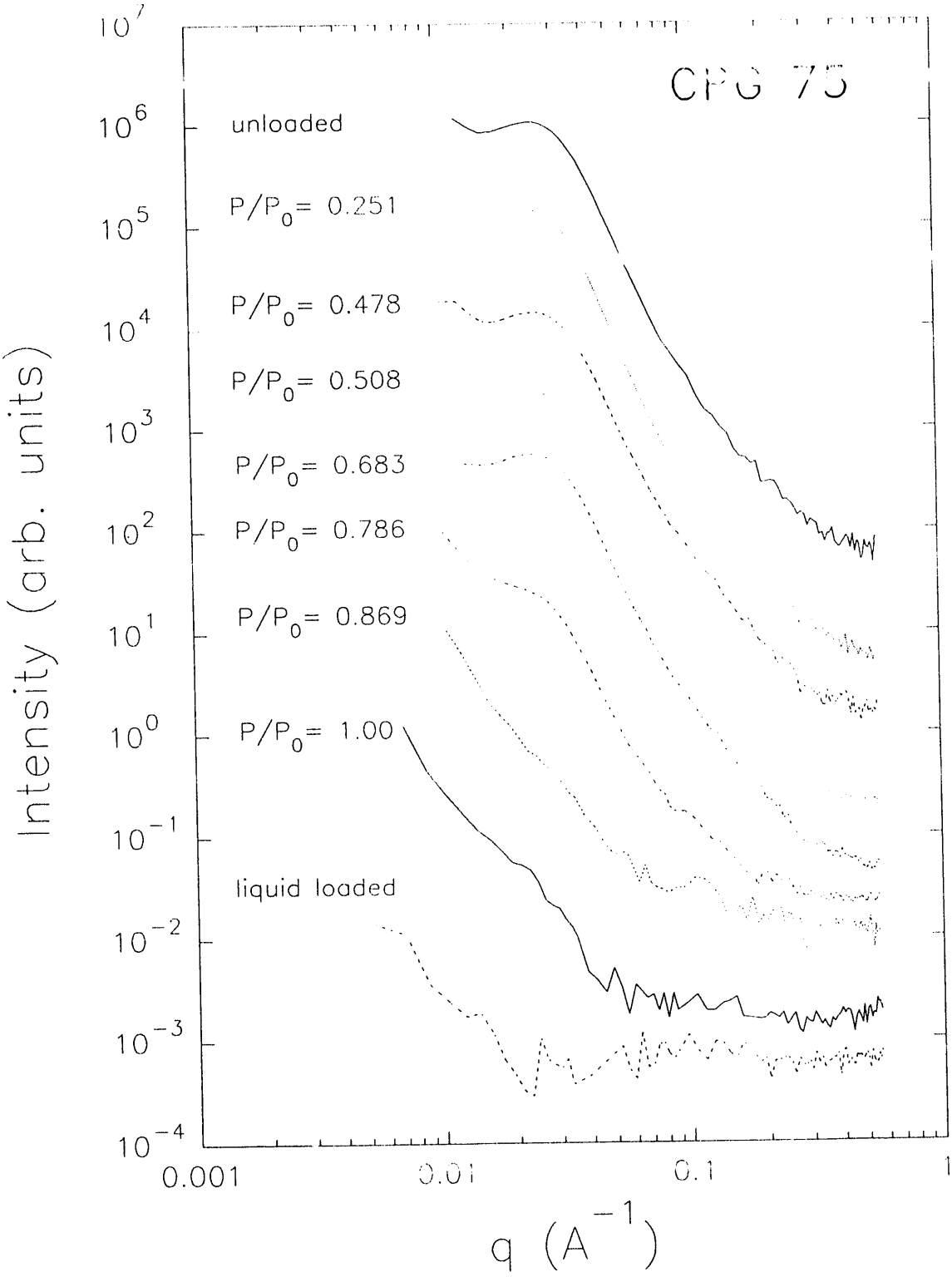

Figure 1 SAXS curves for dibromomethane adsorbed at varying relative pressure in CPG-75.

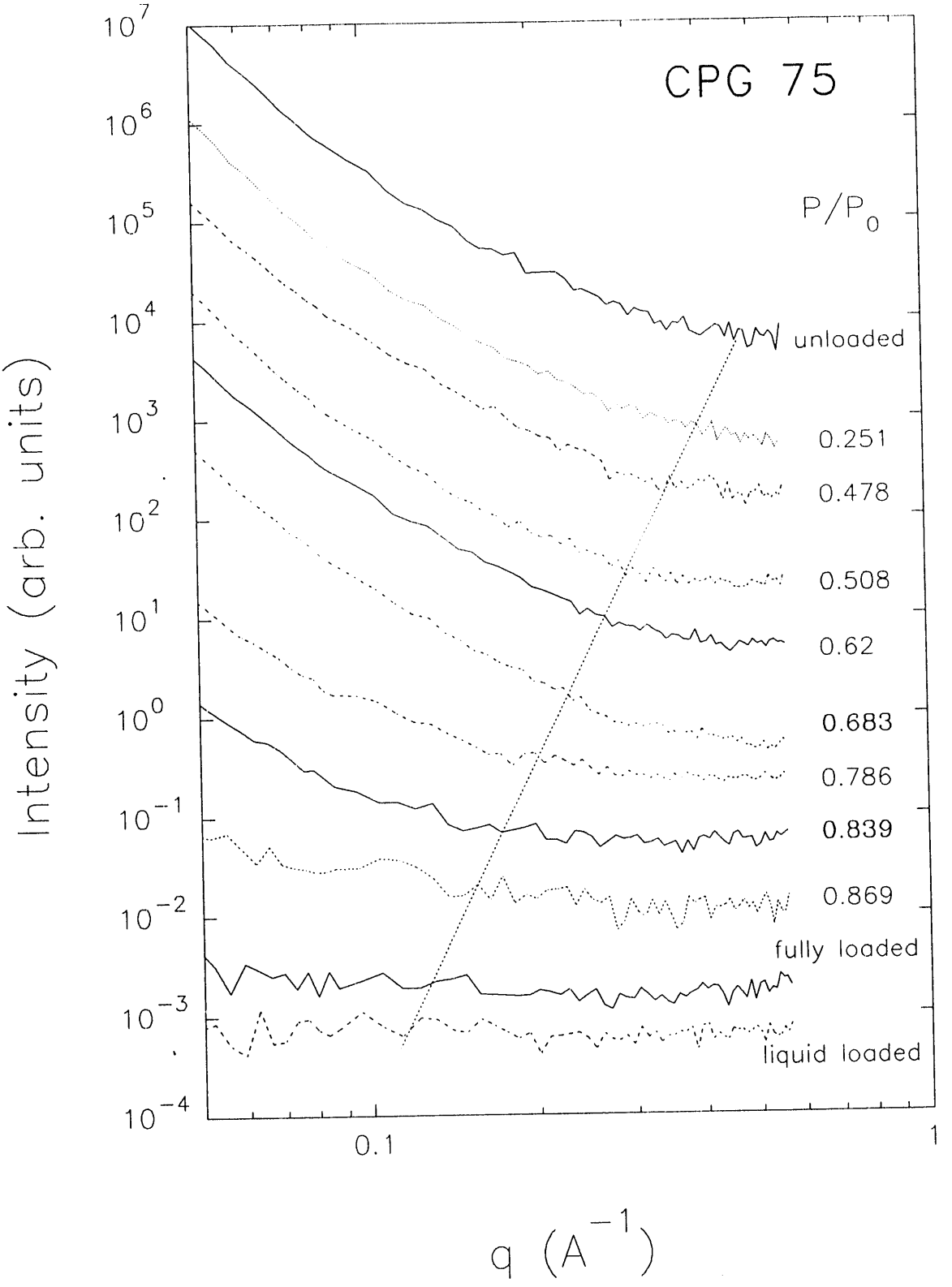

Figure 2 Large Q region for dibromomethane loaded CPG. (line is for comparison purposes)

pressure range was used to obtain more information about the pore filling mechanism, and correlation with the previously obtained high-pressure data was carried out. The combined isotherms are plotted for methane adsorption and carbon dioxide adsorption in Figures 3 and 4. The corresponding Dubinin-Radushkevich plots are given in Figures 5 and 6. Significant nonlinearity is observed which is presumably a result of a nonunifrom adsorption potential arising from either a broad pore size distribution and/or surface chemical heterogeneity. Therefore, Dubinin-Astakov (DA) plots were made for which the coefficient, n, is allowed to vary. These plots are shown in Figures 7 and 8. Values of computed pore structure parameters (surface area, pore volume, etc.) are presented in Table 1.

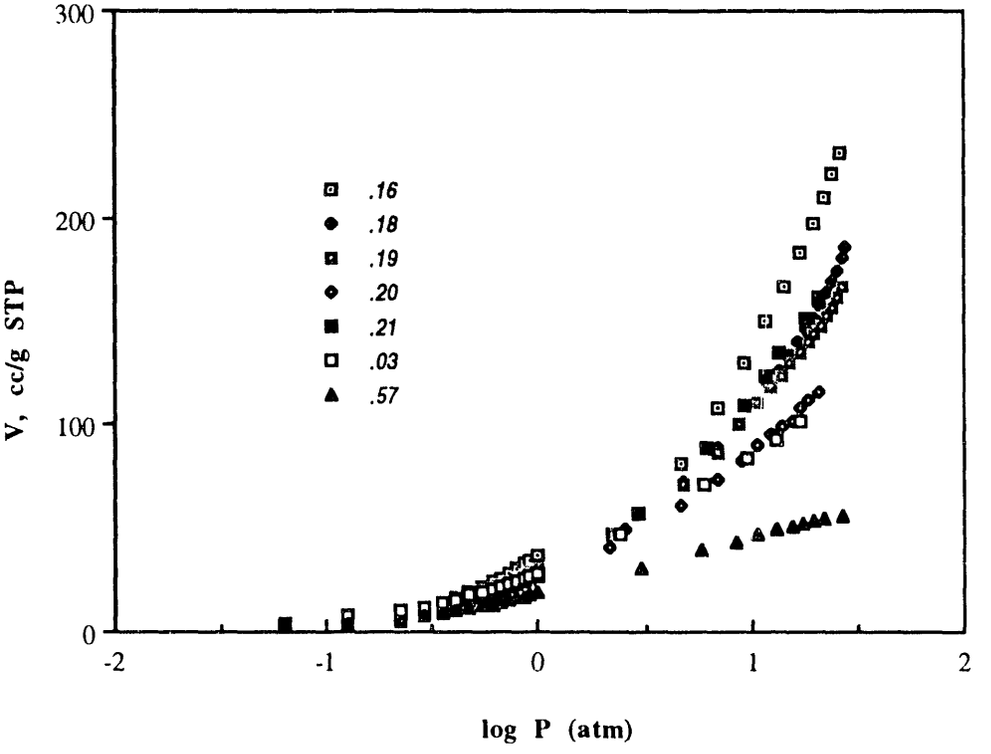

Figure 3 Methane adsorption isotherms on carbons at 295° K.

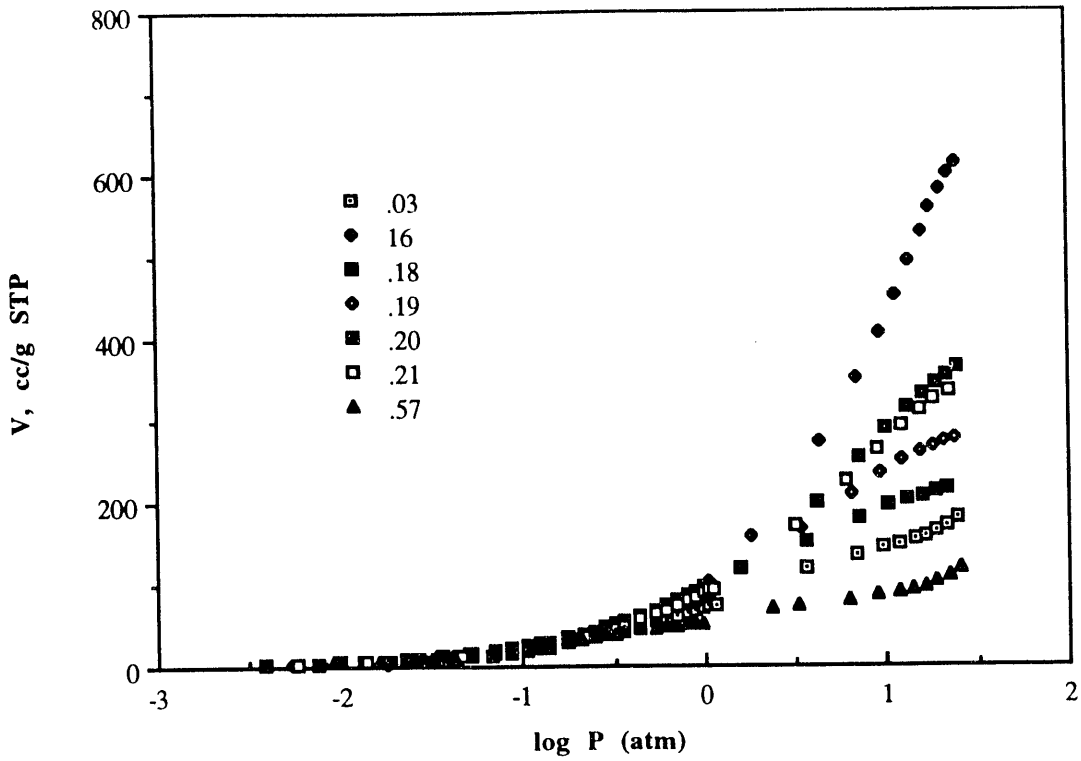

Figure 4 CO2 adsorption on carbons at 273 K

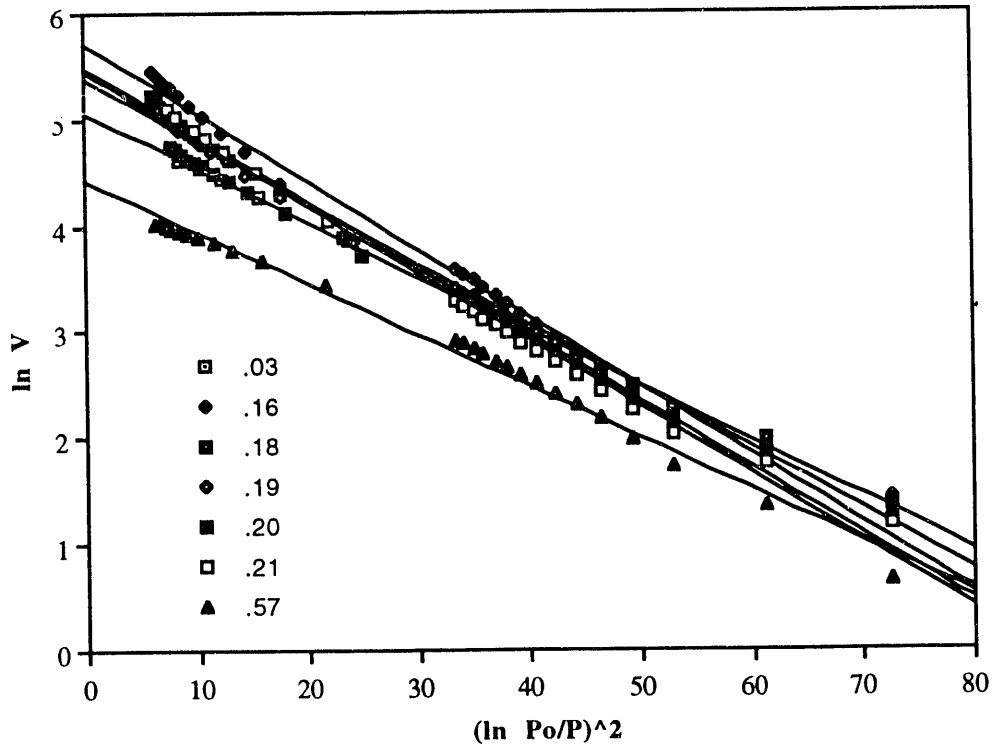

Figure 5 DR plots for methane adsorption

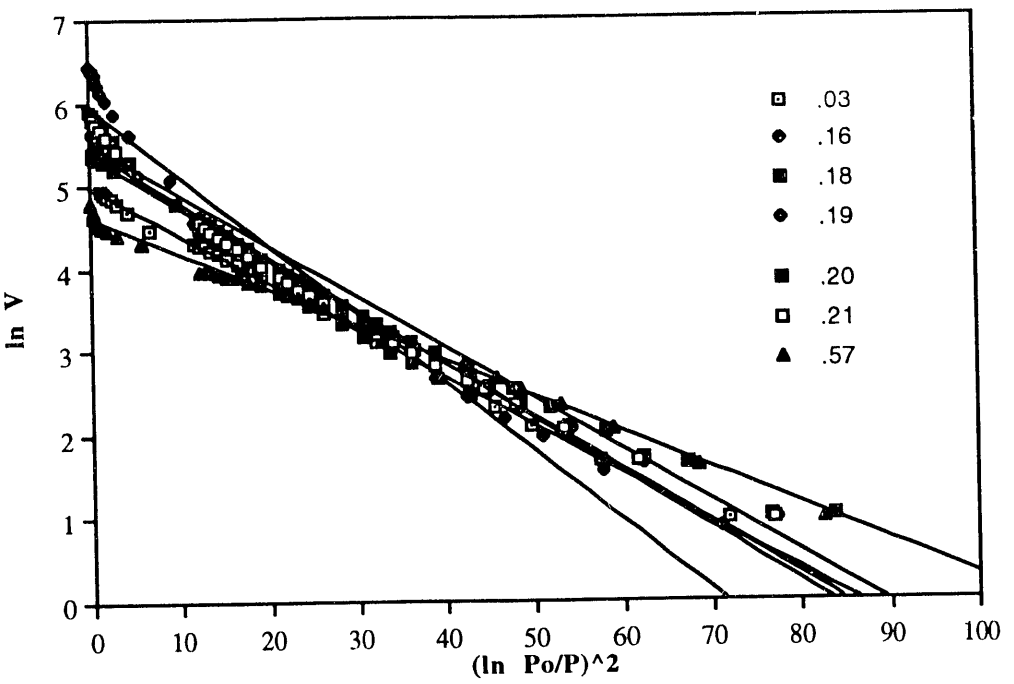

Figure 6 DR plots for carbon dioxide adsorption on carbons

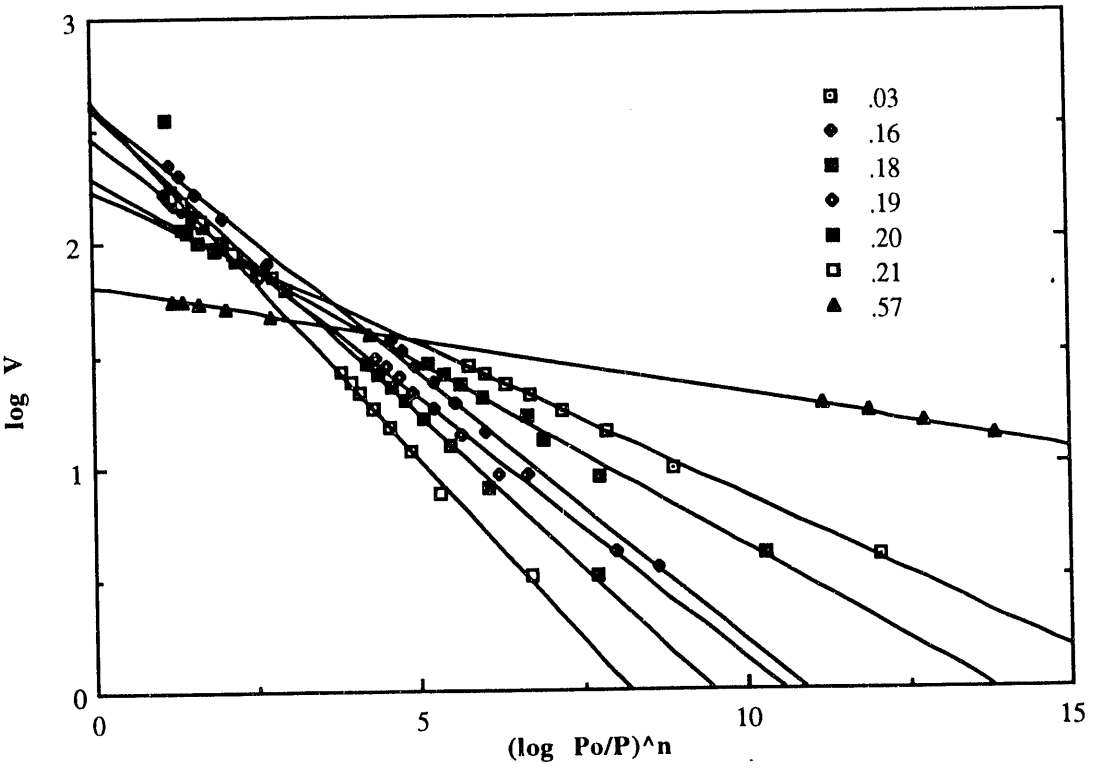

Figure 7 DA plots for methane adsorption on carbons

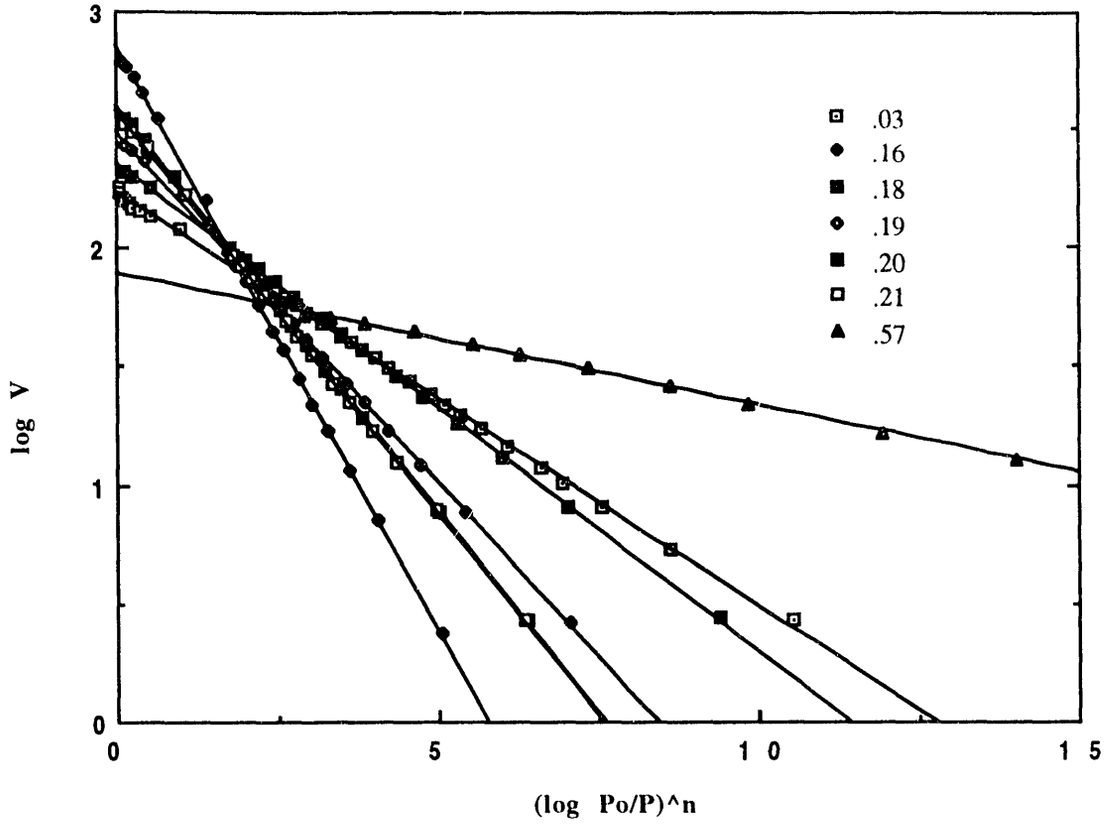

Figure 8 DA plots for carbon dioxide adsorption on carbons

It appears that to obtain accurate estimates of the degree of activation using the DA exponent, it is essential to carry out sorption measurements over a wide range of relative pressures. The values of the DA exponent for CO_2 sorption as reported in the previous quarter changed significantly when the low-pressure data was also fitted to the curve. The new values correlated much better with probe exclusion studies and with surface areas as obtained earlier. In hindsight this is not surprising since the DA exponent is essentially a measure of the (energetic) heterogeneity of the surface, and a true estimate of heterogeneity can only be found by adsorbing over a wide enough range of pressures so that pores of different adsorption potentials are well-represented. Performing the analysis at one end of the pressure range will inevitably result in a skewing of the data towards a particular range of pore sizes.

Nitrogen adsorption was carried out at liquid nitrogen temperature, 77 K, and the resultant isotherms gave further information about the pore structure. Most of the pores were filled at very low relative pressures, so that at a relative pressure of 0.1 pore filling was almost complete. The volume of nitrogen adsorbed at $P/Po \sim 0.995$ was used to determine the pore volume, since at such high relative pressures it is reasonable to assume that the adsorbate is present in the pores in the liquid state. The density of liquid nitrogen being known, it is simple to calculate the pore volume available to nitrogen molecules. The nitrogen pore volume and those obtained from CO_2 sorption (using the liquid density of CO_2 and the extrapolated limiting pore capacity using the DR equation) differed for each of the carbons

studied, and nitrogen pore volumes were higher than the CO_2 pore volumes for most samples. Yet in the case of -071.03 and -058.57, the CO_2 pore volume is higher than the N_2 pore volume, particularly for -058.57, where the difference is almost 100%. This supports our surmise that these two samples contain constricted pores, i.e., pores with small openings. N_2 is unable to penetrate through these openings at low temperatures, whereas the much more energetic CO_2 molecules are able to push there way through into the pore. Further proof of the presence of narrow or constricted pores in sample -058.57 was obtained from the fact that the desorption branch of the N_2 isotherm exhibited low-pressure hysteresis; this means that molecules once adsorbed into the pores are not desorbed even at low relative pressures. Some workers attribute this kind of behavior to the permanent inelastic deformation or swelling of the pores once the adsorbate molecules are trapped in the pores of the adsorbent. When this happens, the molecules are not easily released during desorption. In fact great difficulty was experienced in degassing this particular sample subsequent to the nitrogen adsorption experiments.

TABLE 1 Comparison of results obtained from methane (295 K), carbon dioxide (273 K), and nitrogen (77 K) adsorption

Sample ID, 7461-	DA surf. area CH_4, m^2/g	DA exponent, CH_4	DA surf. area CO_2, m^2/g	DA exponent, CO_2	N_2 BET surf. area, m^2/g	N_2 pore vol., cm^3/g	CO_2 pore vol., cm^3/g
071.03	599	1.9	809	1.81	600	0.3518	0.3543
028.16	1320	1.65	2693	1.24	2652	1.4591	0.1239
071.18	1103	1.56	1663	1.35	1641	0.9382	0.761
071.19	961	1.59	1322	1.45	1097	0.6351	0.5938
071.20	669	1.78	1053	1.68	886	0.5101	0.4679
071.21	1307	1.45	1577	1.39	1487	0.8574	0.7091
058.57	248	2.62	507	2.01	122	0.1022	0.2213

3. NMR Techniques.

Recent progress will be separated into hardware development and implementation and actual NMR data. In the former category, we have just completed the development and testing of a NMR probe system and cryostat that gives us the capability of NMR experiments at temperatures from about 3 to 400 K. The probe system has been tested over the NMR frequency range needed for most of the compounds of interest. The sample size is essentially a cylinder of about 14 mm diameter and 16 mm length. The probe system includes a capillary tube connected to a gas handling system. This allows us to monitor and change the pressure of the gas over the sample. The pressures available are ~10^{-5} torr to ~5 atmospheres. It is our belief that this entire system will allow the greatest flexibility in testing

adsorption, monitoring adsorption properties, and performing in situ NMR using almost any NMR active gas and any porous material.

Most of our work this quarter was using the tubular aluminosilicate, imogolite, as a model porous solid. Imogolite is interesting since it is made up of tubes with an inner diameter of ~0.8 nm which are packed in an hexagonal array. Based on the outside diameter of ~2.5 nm, the openings between three tubes in the array will be ~0.4 nm. Previous work with low pressure nitrogen adsorption has confirmed these sizes as well as the respective volumes of each type of pore. The chemical shift of ^{129}Xe was measured as a function of pressure and outgassing temperature. Previous adsorption work has shown that the small ~0.4 nm pores are not outgassed until temperatures of >250 ^{o}C are reached. Figure 9 is a plot of shift versus pressure. Also included on the plot is a structure for imogolite. The pore size is obtained by extrapolating to zero xenon pressure. For the samples heated to 225 and 250 ^{o}C, the pore size is 0.74 nm. Upon further heating, the pore size increases slightly to 0.78 nm. It is unclear whether this increase is a result of further adsorbed water/dehydroxylation inside the tube or a change in effective tube size as the small pores are emptied of water. However, we see no evidence of xenon having access into the small pores.

In addition to ^{129}Xe, we have also studied $^{15}N_2$ gas adsorbed in imogolite at two different pressures as a function of adsorption temperature. Figure 10 shows NMR spectra as a function of temperature for an imogolite sample loaded at low nitrogen pressure such that only the 0.4 nm pores are filled. At high temperature (128 K), only a single broad peak is observed due to the molecular movement of the N2. At lower temperatures, two peaks are observed. Neither line shape is that expected for frozen nitrogen. This could mean that nitrogen does not freeze in the pores at these temperatures. As the sample is cooled, one peak disappears. Figure 11 shows a similar set of spectra for a sample loaded to higher pressure such that all pores should be filled. Again, a transition from a single broad peak to two peaks to a single peak is observed as the sample is cooled. However, the temperatures at which these transitions occur is significantly different. Although we are not yet able to assign these peaks and understand what their meaning is, we find these results encouraging since the effect is quite dramatic for such a small difference in pore size.

Work planned for next quarter

Our goals for the next quarter include:
1. Correlate adsorption results with SAXS for the carbon samples..

2. Measure adsorption isotherm of dibromomethane on CPG -75 and start contrast-matching SAXS experiments on carbon samples.

3. Continue $^{15}N_2$ NMR experiments of nitrogen adsorbed in porous solids to duplicate the conditions of BET experiments. This will include using a series of specially prepared silica xerogels which will allow us to vary the pore size over a wide range (1-50 nm) with no change in surface chemistry.

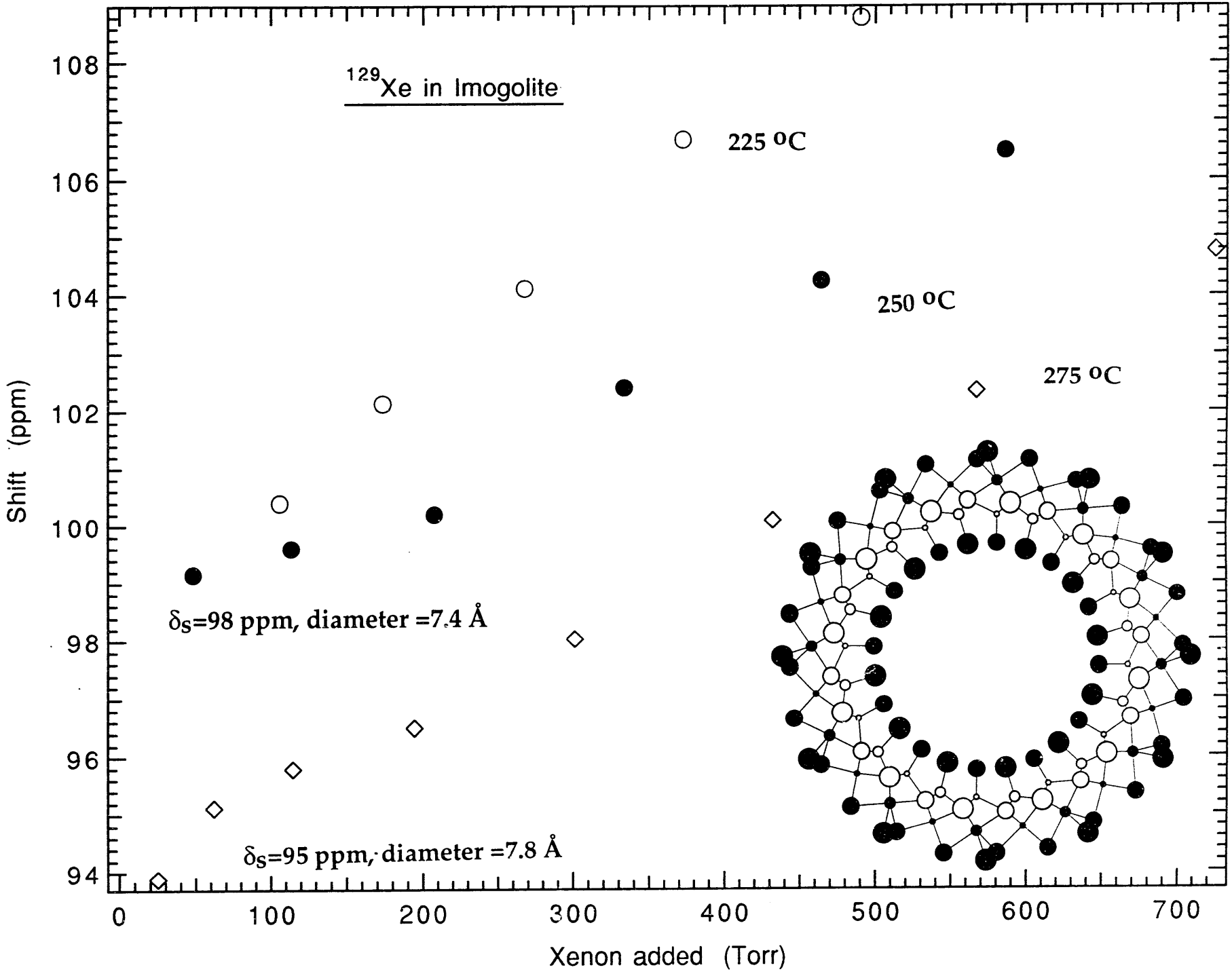

Figure 9 Xenon chemical shift in imogolite as a function of outgas temperature.

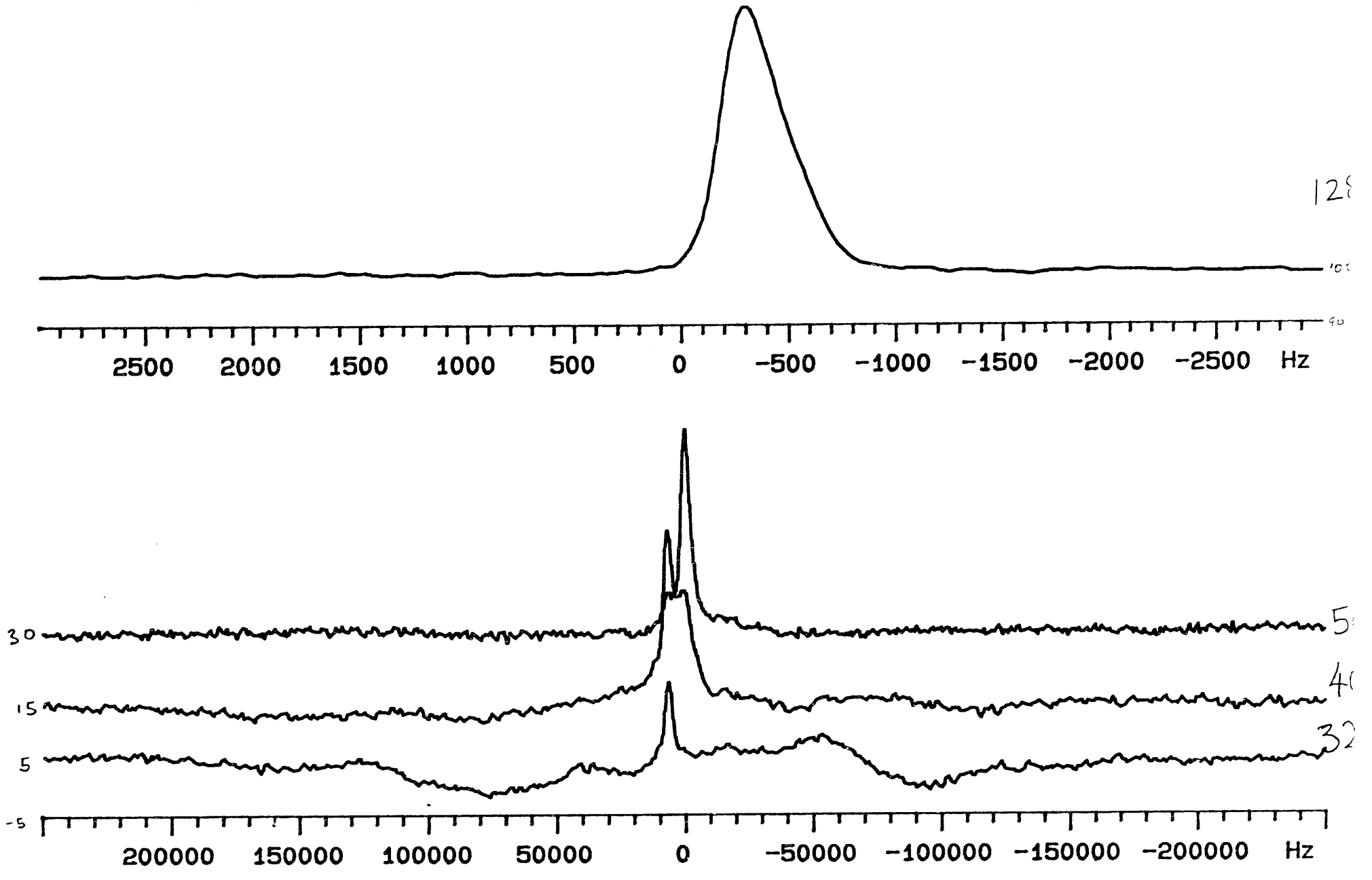

Figure 10 Nitrogen spectra for nitrogen adsorbed in imogolite at low pressure in imogolite

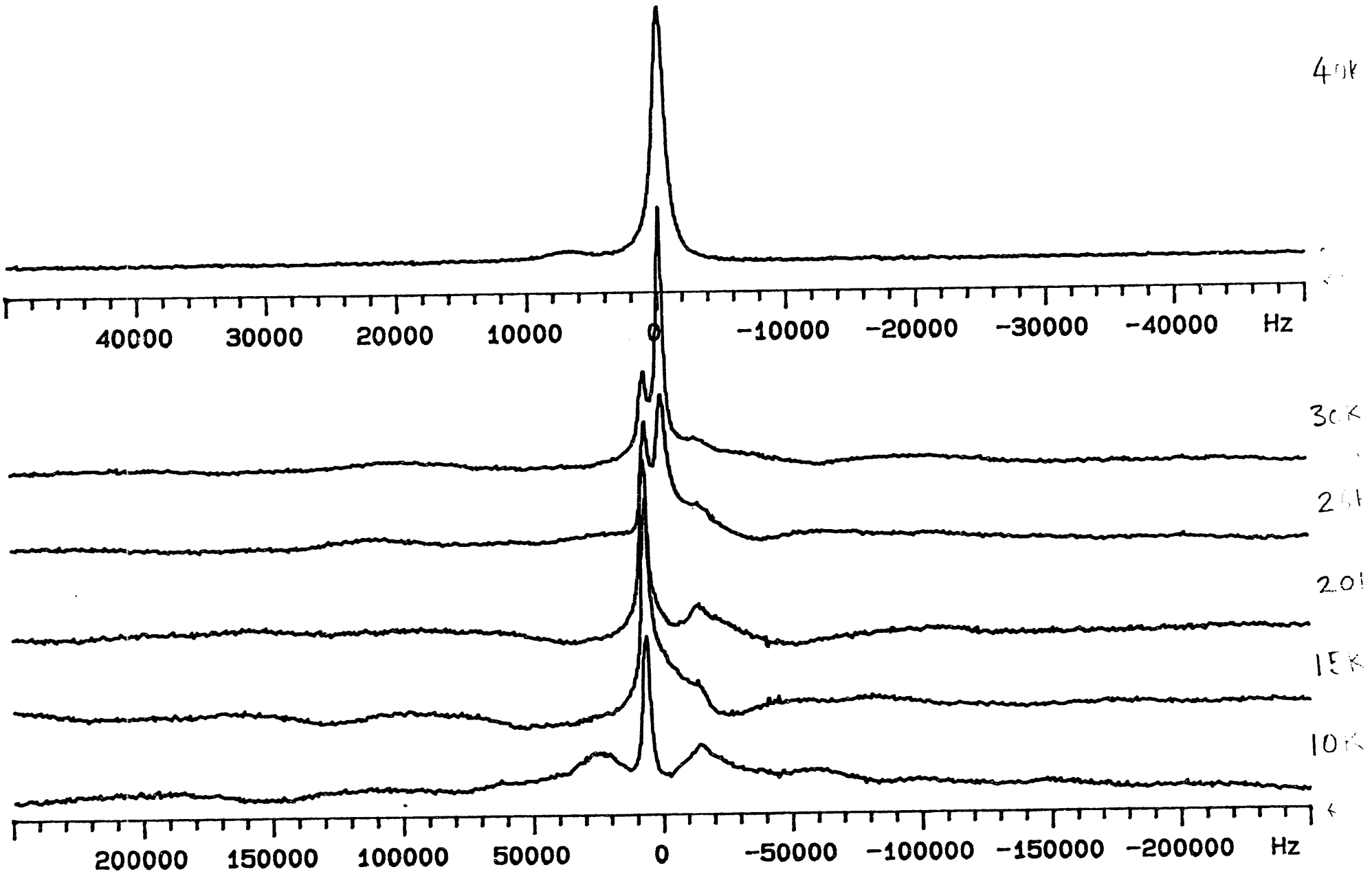

Figure 11 Nitrogen spectra for nitrogen adsorbed at high pressure

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