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NMR MEASUREMENT OF PORE STRUCTURE

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INTRODUCTION

For some time, we have been working on various methods of using Nuclear Magnetic Resonance (NMR) as a tool to measure pore sizes, pore size distributions, and pore structures. The reason for this effort is the realization that NMR is sensitive to short range order and the NMR relaxation times and chemical shifts are potential sources of exactly the type of information required to determine the structure of micropores.

Early in the history of NMR, it was recognized that the NMR relaxation times of fluids in restricted geometries are sensitive to pore size¹. This phenomenon arises because the relaxation time of molecules in contact with the surface of the pore is much shorter than those in the bulk. There is rapid exchange between molecules on the wall and those in the bulk resulting in an average relaxation time which can be related to the surface to volume ratio of the pores. Considerable effort has been dedicated to understanding this effect and to deriving the proper mathematical formalism to extract pore sizes and pore size distributions from measurements of NMR magnetization²⁻⁵.

More recently, it was realized that the chemical shift of ^{129}Xe can be related to pore sizes in closed pore systems as well as in open pore materials such as zeolites^{6,7}. This technique is relatively easy, the NMR sensitivity is high, and the application requires only simple mathematical analysis. As a result, ^{129}Xe NMR has been applied in a large variety of materials from clathrates and zeolites through ceramics and even in coals where the association of the shift with pore size is tenuous, at best. There is at least one report in the literature, in a silica with large pores, where the measured shift is clearly inconsistent with the theory as applied to zeolites⁸. The authors attempted to explain the data in terms of surface roughness. There have been several other critical studies of Xe shift measurements of pore sizes and work continues with the goal of understanding the basic physical chemistry underlying these shifts and giving them a quantitative interpretation^{9,10}.

Several years ago, we decided to pursue ^{129}Xe NMR as a pore measurement technique in hopes of understanding the details of the system. We have also investigated other magnetically active nuclei and small molecules as probes of pore size and adsorption sites. This manuscript is a description of some of our attempts. It includes systems in which we were successful in measuring pore sizes and cases in which we were unsuccessful. We will discuss several "freezing" experiments in which we reduced the temperature well below the freezing point of the pore fluid. This is analogous to thermoporometry using NMR as a detector of the phase transition¹¹. The distinction between NMR and thermoporometry is that in the latter case one determines the temperature at which a first order phase transition takes place and in the NMR measurements one

observes the NMR lineshape which indicates the temperature at which molecular motion becomes "slow", where slow is defined as having motional correlation times longer than about 10^{-3} s. These experiments do not yield quantitative information about pore sizes or pore size distributions but they add to our understanding of the physical properties of molecules in confined spaces. They are also useful in obtaining information about relative pore sizes. We will also describe a few experiments with "quadrupolar" nuclei in which we failed to obtain useful data. These are presented to aid the readers and, hopefully, prevent others from making the same ill-fated measurements.

EXPERIMENTAL

All NMR data were taken on a Varian Unity 400 spectrometer operating at an applied magnetic field of 9.4 T. A special probe was constructed for this work. It is based around an Oxford model CF1200 cryostat. The probe itself is of a transmission line design¹². Samples were sealed in 16 mm o.d. pyrex tubes, sealed to a 1 m long pyrex capillary which can be readily connected to a gas handling system. This configuration allows us to bake out the sample to about 750 K under vacuum, insert it in the NMR spectrometer and then control the pressure and chemical composition of the gases on the sample without removal from the spectrometer. The temperature, during NMR experiments, can be controlled over the range from about 3 to 430 K. Temperature control is achieved with an Oxford temperature controller and measured with a carbon-glass resistor. Once stabilized, temperature fluctuation and accuracy is better than 0.1 K. With this system we can effectively perform adsorption isotherm measurements concurrent with the NMR measurements.

The samples reported in this study are: imogolite¹³, commercially available sodium Y zeolite, and an aerogel, and xerogel which were prepared through gelation of TEOS¹⁴. The samples were dried at temperatures from about 520 K for the imogolite to over 670 for the zeolite. They were dried for at least 16 hours at temperature under a vacuum of less than 10^{-4} torr.

The gases used were "normal" xenon gas which was purified slightly through condensation and freeze thaw cycles, $^{13}\text{C}\text{O}_2$ (99.9% enriched) purchased from Cambridge Isotope Labs, and $^{15}\text{N}_2$ which was obtained from the Los Alamos stable isotope separation facility.

RESULTS AND DISCUSSION

Xenon Shift Measurements

The earliest applications of this technique can be attributed to Ripmeester⁶ and Fraissard⁷ who applied ^{129}Xe chemical shift measurements at 26° C to understanding the pore sizes and character of clathrate and zeolite pores, respectively. Since those reports, a number of other groups have attempted to use this technique¹⁵⁻¹⁸. In zeolitic systems, Fraissard and coworkers have developed a theory which relates the ^{129}Xe chemical shift at infinite Xe dilution, δ_∞ , to the mean free path of Xe l , which can, in turn, be related to the pore dimensions with certain assumptions about the pore geometry. This results in a rather simple equation:

$$\delta_\infty = 243 \times \frac{2.054}{2.054 + l}$$

Where δ_∞ is the ^{129}Xe shift, corrected for Xe-Xe interactions and l is the mean free path. Work by Conner, *et al.*⁸ indicates that there are problems with an indiscriminate application of this mean free path model and resulting equation to the determination of pore sizes. In that work the measured chemical shift was much greater than expected for the packed silica material.

We have duplicated measurements on several zeolites reported in the literature. In most cases, our experimental setup allows us to go to significantly lower pressure than previously reported. Our results on zeolites are unremarkable in that they substantially agree with reported data. We note that for these hygroscopic materials, sample treatment can significantly change the NMR shifts measured.

We have dedicated a significant effort to measurement of the pore size of synthetic imogolite, a tubular aluminosilicate with a gibbsite structure. The gibbsite sheet is essentially rolled with the SiO_4 tetrahedra to the inside of the cylinder. The cylindrical micropore created has a diameter of 0.7 nm¹⁹. As synthesized, this imogolite is ordered in having the tubes packed in parallel bundles forming a sort of microcrystallite. This implies that there are smaller micropores between the tubes which we estimate to be about 0.3 nm in size. These are so small that Xe (atomic diameter = 0.44 nm) cannot enter them. Using the above equation and computing the pore diameter for a cylindrical pore, we obtain 0.75 nm from the Xe shifts. This result is satisfying but the sample is very similar to zeolite samples so we might expect to apply the mean free path model without problems.

We have also applied ^{129}Xe chemical shift measurements to sol-gel prepared silicas. These samples are prepared from tetraethoxysilane, followed by controlled aging, and drying from pore fluids of varying surface tension¹³. We report here on a xerogel dried from tetrahydrofuran and an aerogel prepared by exchanging the normal pore fluid (H_2O EtOH) with liquid CO_2 and drying above the critical point. This results in a xerogel with a pore radius of about 4.5 nm and an aerogel with a pore radius of about 30 nm. A straightforward application of Fraissard's "mean

free path model" would result in ^{129}Xe shifts of about 22 and 3.3 ppm for the xerogel and aerogel respectively. In fact we measure shifts of around 100 ppm for both samples. Additionally, the shift as a function of Xe loading is not linear, as predicted by the theory. This non-linearity agrees with Cheung's conclusions that samples with distributions of pore sizes will give curved plots for the ^{129}Xe shift as a function of xenon loading. We also attempted to measure the pore size of pores in a carbonate rock obtained from Texas A&M University. This geological sample is of interest because of its potential as an oil bearing mineral. We measured an infinite dilution shift of about 3.8 ppm corresponding to a pore radius of 13.4 to 26.3 nm, depending on the model chosen for the pore geometry. We are assured that the actual pore radius is about 200 nm.

Our results on the xerogel and aerogel agree with Conner *et al*⁸, indicating that one must apply caution in interpreting ^{129}Xe chemical shift data for samples which are not very similar to zeolites. It is possible that Conner's interpretation of the anomalously large measured shift is correct...the surfaces are very rough and Xe atoms spend a large amount of time adsorbed in small pockets. This would skew the results towards small pores. On the other hand, the explanation may be simply that the details of the mean free path model are incorrect and ^{129}Xe chemical shifts reflect pore sizes only in a limited range of sample composition and pore size, *e.g.*, from about 0.5 to 1.5 nm. These results certainly call into question ^{129}Xe measurements of pore sizes in very different materials such as carbons and coals. In such samples, the very different pore shapes and pore wall physics would lead one to believe that the empirical equations, derived for zeolites, could hardly be expected to apply even if the basic model is correct. Carbons have an additional difficulty in that they are invariably paramagnetic and the paramagnetism might be expected to produce significant shift effects. We are continuing work on large pore materials, including a variety of sol gel prepared silicas and porous glasses with the aim of understanding the effects of pore wall roughness and perhaps the extent to which the mean free path model can be applied in large pore materials.

Xenon Freezing

Cheung and coworkers have studied the NMR of ^{129}Xe in porous materials at 1.41 K²⁰. They observed the changes in line shape associated with the gas liquid transition in zeolites with large pores and in other porous materials. This can be compared to thermoporometry in which the liquid solid transition of pore water is monitored calorimetrically. The goal of thermoporometry is to relate the freezing point depression to the pore size¹¹. Freezing is a cooperative phenomenon which really requires a bulk liquid. In a system where the pores are so small that all liquid molecules are effectively on the walls of the pores, the thermodynamic concept of freezing in a bulk like liquid does not apply. On the other hand, if we observe the

^{129}Xe NMR signal as a function of temperature we may draw conclusions about density, mobility, and pore size from the chemical shift and relaxation times.

Figure 1 contains the ^{129}Xe NMR spectra of xenon in imogolite at about 640 torr near the freezing point of bulk xenon. Our view of this system is that xenon exists in the micropores of the imogolite and in the macroporous space surrounding the "crystallites". At 162 K, just above the freezing point of the bulk liquid (161.3 K) we see a spectrum indicative of liquid xenon and of xenon in the micropores. As we go from just below the freezing point down to 157 K the spectrum does not change significantly. It is indicative of bulk frozen xenon and xenon in the micropores. With decreasing temperature, we see the chemical shifts consistently becoming more deshielded as expected. At 156 K all of the bulk liquid has frozen. The slight asymmetry in the solid peak we attribute to xenon on the external surfaces of the crystallites. If we continue to lower the temperature, the xenon in the micropores never reaches a chemical shift indicative of bulk freezing. The increased linewidth of the Xe in the micropores is indicative of decreased motion. We interpret this to be due to heterogeneity in the detailed site structure of the different xenon atoms in the micropore. As the temperature is lowered, a given xenon atom cannot sample as many different sites and the NMR line is inhomogeneously broadened. It is curious that the resonance for Xe in micropores stays relatively symmetrical. In analogy to ^{129}Xe NMR in clathrates, we might have expected to see evidence of chemical shift anisotropy at the lower temperatures. We take this to indicate that Xe atoms in the micropore retain some mobility within a "cage" so they collide with the walls of the pore and with adjacent xenon atoms. This set of data confirms our preconception that molecules in small pores or on the walls of a pore do not "freeze" in a normal fashion.

Freezing of CO_2 and N_2

In our studies of imogolite, we thought that it would be interesting to investigate linear molecules in the long cylindrical micropores. We were also interested in putting a small molecule into the channels between the imogolite cylinders. One of the goals was to obtain a spectrum which demonstrated a chemical shift anisotropy. We know that in bulk N_2 or CO_2 the NMR lineshape is symmetrical down to quite low temperatures due to rotation of the molecules. However, in a cylindrical pore, nearly the size of the molecules, we would expect the molecular electric quadrupole to cause the rotational motion to slow down. This should result in observation of a well known chemical shift anisotropy (CSA) pattern²¹. Figure 2 contains a series of ^{13}C spectra of CO_2 in imogolite as a function of temperature. The upper spectrum is the CSA pattern expected when motion is stopped. This spectrum was taken using a "solid echo" NMR pulse sequence which only results in signal from molecules which are frozen. The spectrum

immediately below it is the Fourier transform of a Bloch decay which should give signals from all CO_2 molecules in the sample. It is the superposition of the CSA spectrum from the solid and a rather broad peak due to mobile CO_2 molecules. As the temperature is raised, we simply see that the "liquid" peak becomes stronger and the solid one weaker. At 150 K all that is observed is a fairly narrow resonance due to mobile CO_2 .

Normal nitrogen adsorption measurements of surface area and pore size failed to quantify the small pores between the imogolite tubes. This was due to the fact that those pores are so small, equilibration time is very long, and the equilibrium pressure is below that detectable by the pressure transducers. However, we attempted to use ^{15}N NMR to investigate the adsorption of nitrogen in this system as a function of temperature. Figure 3 contains the ^{15}N spectra of nitrogen at a high loading of nitrogen. The large peak at 40 K is indicative of liquid N_2 in micropores. The minor intensity at about 180 ppm in that spectrum is the indication of a nitrogen CSA pattern just starting to appear. As the temperature is dropped, we start to see the loss of intensity in the liquid peak and an increase in the solid CSA pattern. At the lowest temperature we see indications of a split CSA pattern from the peak at about 200 ppm. The CSA pattern is not as well defined as the one for CO_2 in figure 3 because of instrumental difficulties with such a broad line at the low resonance frequency of ^{15}N . The apparent splitting of the pattern is probably due to ^{15}N - ^{15}N magnetic dipole interactions. Figure 4 contains ^{15}N spectra of the same sample but at a lower loading of nitrogen. In this case we see that the majority of the N_2 freezes at 40 K, a much higher temperature than at high loading. We attribute this to nitrogen molecules in the very small pores between the imogolite tubes. In this case, the space is so confined and the electric quadrupole and van der Waals forces are strong enough to stop the tumbling of the nitrogen molecules at a much warmer temperature than in the larger pores of imogolite.

Quadrupolar Nuclei

This work was performed in analogy to low field NMR relaxation time measurements of pore sizes as exploited by Smith⁵ and Halperin⁴. In NMR relaxation measurements of pore sizes, it is known that pore sizes can be determined from the average relaxation time, T_1 , of the pore fluid. The basic concept is that molecules on the wall of the pore have a much shorter relaxation time than those in the center of the pore which have relaxation times equal to bulk fluid. There is rapid movement of molecules from contact with the wall to "bulk" positions. It is not necessary to know the mechanism of relaxation on the wall, only that the relaxation time be much shorter. It is also found that the relaxation time for those molecules in contact with the wall is a function of the pore fluid and the character of the pore wall. We concluded that if we were able to use a

quadrupolar nucleus where the mechanism of relaxation would always be quadrupolar it might be possible to select molecules where the detailed character of the wall is unimportant.

To that end, we have performed several NMR experiments using ^{131}Xe at different temperatures and $^{14}\text{N}_2$ at 77 K as probe molecules. In both cases, we found that the linewidth is so broad that we were unable to obtain an interpretable spectrum. This results from the rather large quadrupolar moment and slow molecular motion that obtains with these probe molecules in contact with the wall.

CONCLUSIONS

Our original goal, to discover a completely general NMR technique for measuring pore size distributions, has not been realized. Such a goal may not be possible. However, it is clear that there is a great deal of information about molecular motion and interactions available through interpretation of variable temperature NMR experiments. This is true because the NMR technique is sensitive to short range interactions (on the order of 1 nm or less) and to molecular dynamics in the range of 10^{-2} to 10^{-6} s. The work on xenon adsorption and freezing, N_2 adsorption, and CO_2 adsorption reported here is a survey of the potential of these techniques. We are continuing to pursue these experiments in more detail to complete our understanding of the basic physical chemical phenomena and hopefully to obtain better pore size measurement techniques for microporous materials. Our present view is that such techniques are powerful but require experienced practitioners of Nuclear Magnetic Resonance as well as considerable knowledge of other pore characterization techniques.

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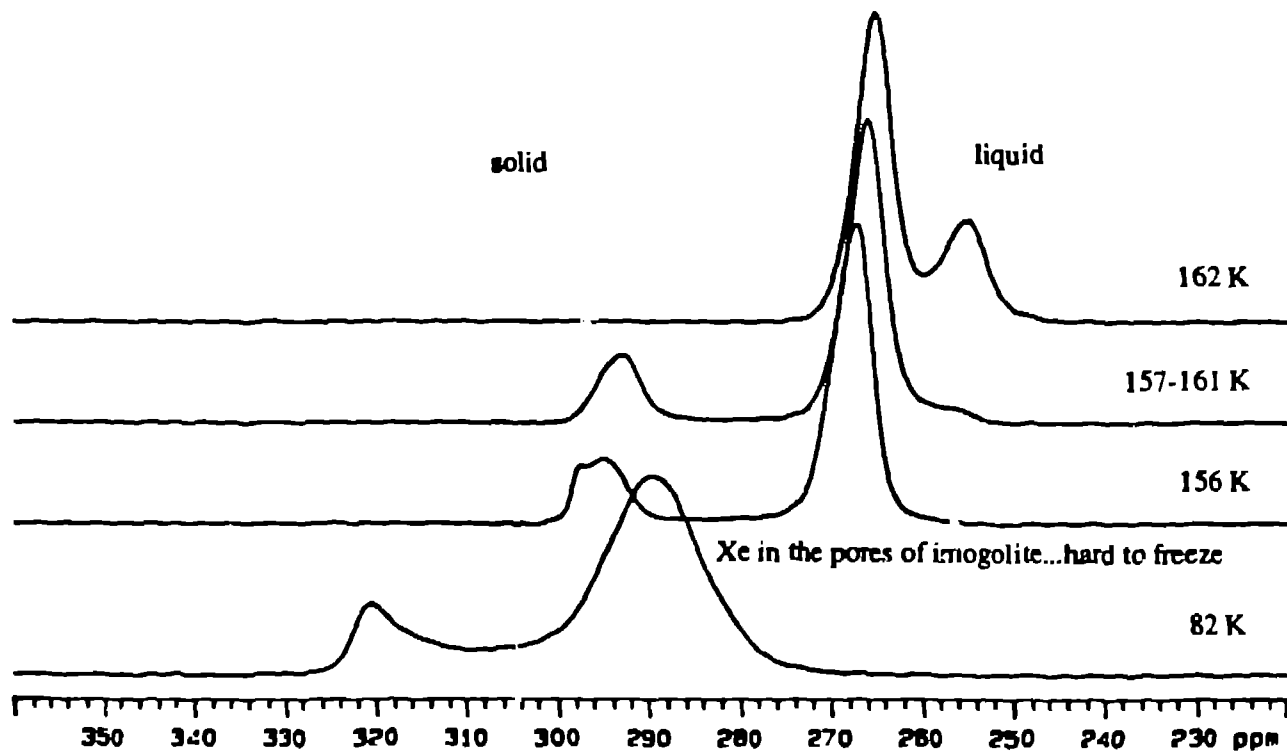
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FIGURE CAPTIONS

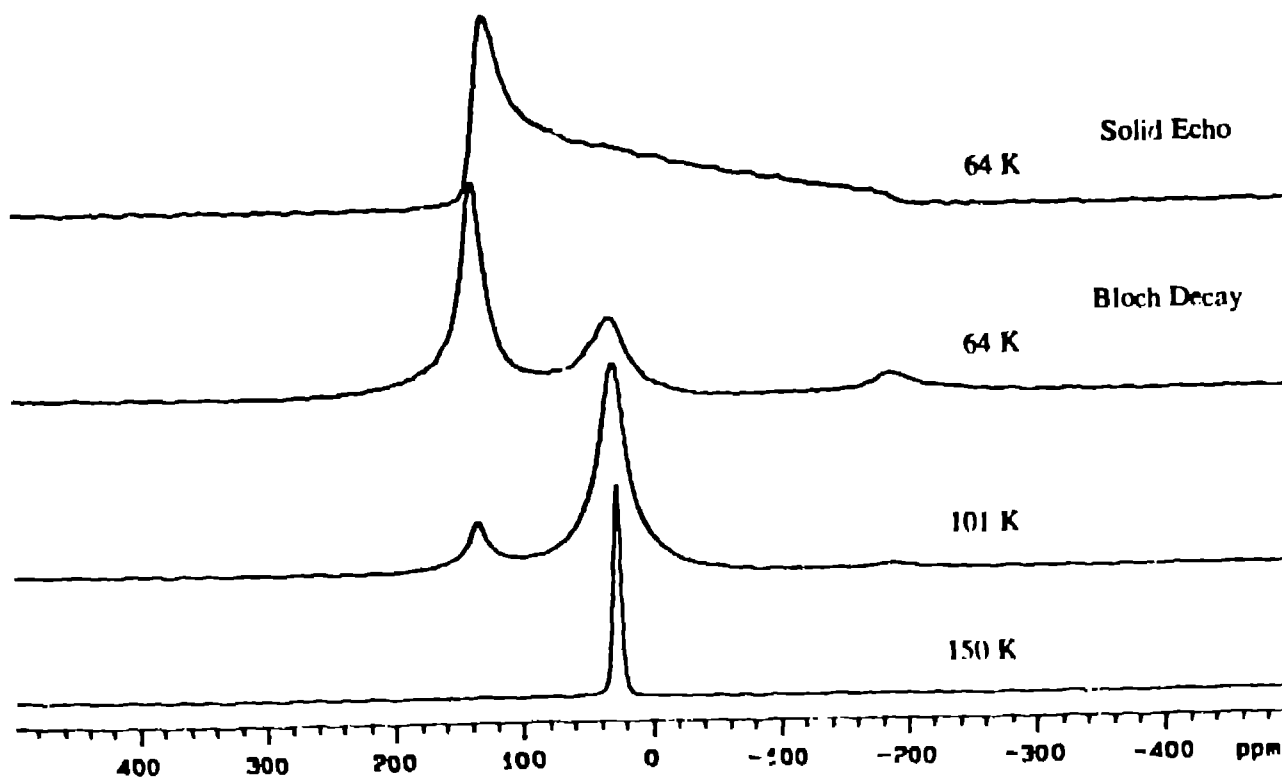
- Figure 1. The ^{129}Xe NMR spectra of xenon in synthetic imogolite at different temperatures.
- Figure 2. The ^{13}C spectra of CO_2 adsorbed on synthetic imogolite at very high loading at different temperatures.
- Figure 3. The ^{15}N spectra of N_2 adsorbed on synthetic imogolite at very high loading at different temperatures.
- Figure 4. The ^{15}N spectra of N_2 adsorbed on synthetic imogolite at low loading at different temperatures. The loading was calculated to fill the very small pores prior to entering the larger pores of the imogolite.

Xenon in Imogolite

Xe in micropores



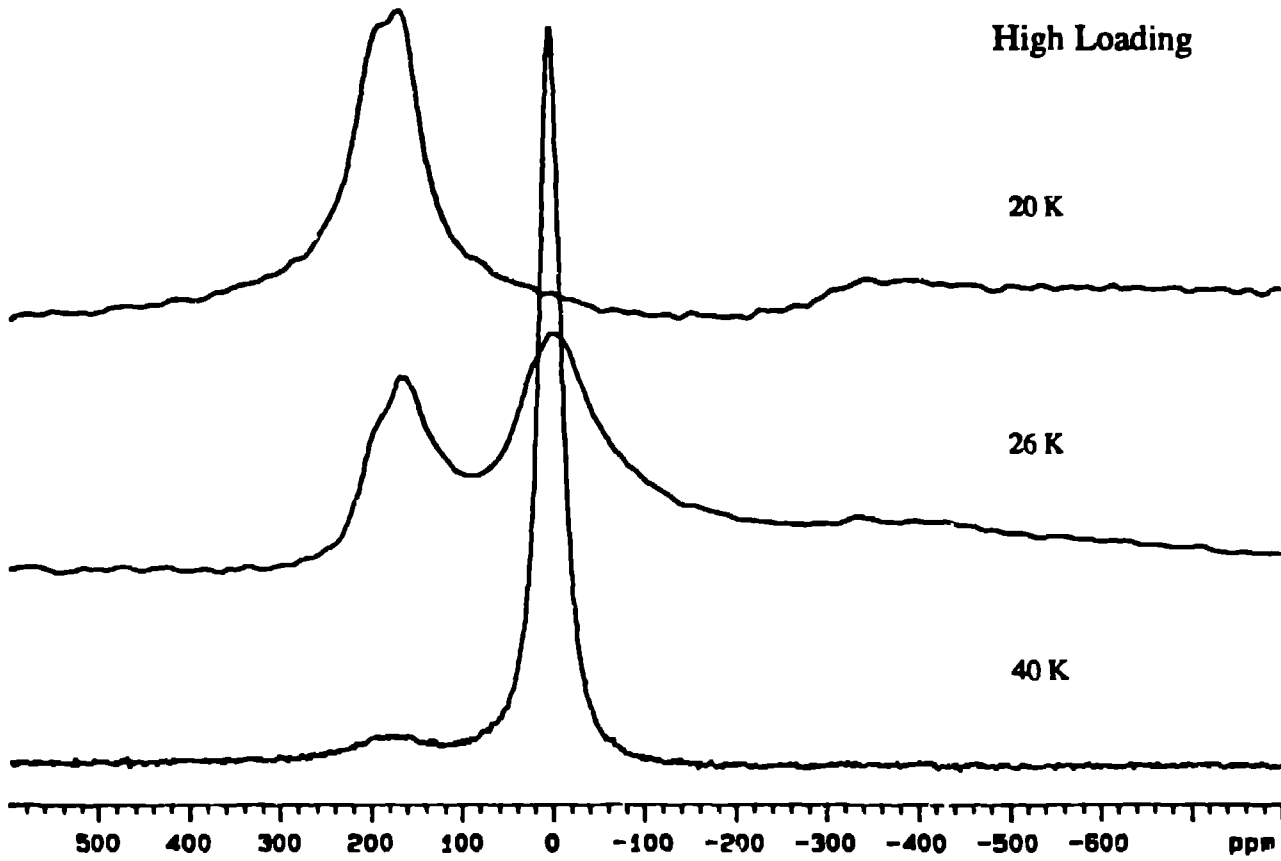
¹³CO₂ on Imogolite Full Loading



16 5

$^{15}\text{N}_2$ on Imogolite

High Loading



$^{15}\text{N}_2$ on Imogolite

Low Loading

