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Structure of D_2 in zeolite

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We have measured the structure of D_2 adsorbed in zeolite 13*X* at temperatures in the range 5.5 to 80 K at a variety of fillings. We find that the D_2 molecules adsorb into well-defined adsorbtion sites in the zeolite structure. Two distinct adsorbtion sites, with binding energies on the order of 40 and 80 K, have been identified. No evidence for bulklike liquid or solid behavior of the D_2 adsorbed in the pores has been observed. Once the adsorbtion sites are saturated D_2 is no longer adsorbed into the pores and forms a bulk phase on the surface of the zeolite.

I. INTRODUCTION

Molecular hydrogen, as a boson, has the potential to become a superfluid at low temperatures.[1,2] This has motivated much recent work since it would offer the possibility of studying superfluidity in a strongly interacting Bose system other than liquid ^{4}He. Estimates of the superfluid transition temperature for liquid H_2 give values on the order of 4–6 K, comparable to those in liquid helium.[1] Unfortunately, because of the strong interactions of hydrogen molecules, formation of the solid phase occurs at 13.8 K in the bulk[3] and preempts any transition to a Bose-condensed phase.

Suppression of the liquid-solid transition temperature, known as supercooling, which occurs for finite-size samples, has prompted many attempts[4–6] to observe a superfluid phase transition in finite-size samples of liquid H_2. Sufficiently large supercoolings would allow Bose condensation to be observed. A variety of methods have been applied to limit the size of the H_2 sample.[4–11] One of the most widely used is the confinement of hydrogen in porous media, such as porous glasses[4,7,11,12] and zeolites.[5] The suppression of the liquid-solid transition in these porous materials is expected to vary inversely as the pore size,[13] and so much of this work has centered on materials with pore sizes below 100 Å. For example, measurements of H_2 in Vycor, a porous glass with a nominal 70 Å pore size, have observed suppression of the liquid-solid transitions by 3–4 K.[4,6,7] Such results are promising, but do not offer sufficient supercooling to allow a transition to a Bose-condensed phase to occur.

Attention has recently focused on zeolites because of their extremely small and regular pore structure. Zeolites are crystalline materials, usually composed of an alumino-silicate backbone, which have a regular structure of pores on the order of 10 Å in diameter connected by channels on the order of 8 Å in diameter. Thus they offer much smaller pores than available with porous glasses and corresponding larger supercooling. Recently, Rall, Brison, and Sullivan[5] reported NMR measurements of H_2 adsorbed in zeolite 13*X*, where the transition was significantly suppressed with respect to the bulk. They observed a supercooling that depended on the concentration of the $J=1$ species and, when extrapolated to zero $J=1$ concentration, was on the order of 8 K, large enough that Bose condensation might occur.

In this paper we describe neutron-diffraction studies of D_2, an isotope of H_2, adsorbed in zeolite 13*X*. D_2 and H_2 have similar interactions and differ only in their mass. Thus studies of D_2 should also provide insight into the behavior of H_2 in zeolites. Neutron diffraction is an ideal probe since it provides direct information on both the long- and short-range correlations in condensed systems,[14] which determine the nature of the liquid and solid phases in the pores.

Our results indicate that D_2 is strongly adsorbed in specific binding sites in the zeolite structure. Since the statics and dynamics of the molecule are dominated by the zeolite-D_2, rather than D_2-D_2, interaction, no liquid-solid transition exists. Instead, the D_2 molecules should be viewed as an integral part of the low-temperature structure of zeolite and not as a weakly adsorbed system. Since no liquid phase, in the common sense, exists, there is no reason to expect that Bose condensation would ever

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occur.

We have identified two distinct adsorbtion sites within zeolite with binding energies of the order of 40–80 K. Upon filling, molecules are adsorbed into these sites until they are saturated. Further filling leads to the formation of bulk D_2 outside the zeolite structure. Thus, after saturation of the strong binding sites, the pores appear to be totally filled. No additional pore volume is available for a liquid phase to form in the pores.

II. EXPERIMENTAL DETAILS

The neutron-diffraction measurements were carried out using the PHOENIX spectrometer at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. The instrument was configured as a high-resolution powder diffractometer for these measurements. The instrument consisted of a 14-m incident flight path and two final flight paths: one with detectors at 145° and 4 m from the sample and the other with detectors at 50° and 2.5 m from the sample. The observed scattering was consistent between the two flight paths. The high-angle flight path as a result of its longer length, provided higher-resolution results and only those results are presented here. The low-angle flight path provides essentially equivalent data, but with poorer resolution. The data, obtained as neutron counts versus time of flight, are corrected for the incident beam spectrum, measured using a low-efficiency detector, and converted to $S(Q)$ using standard techniques.[15] Since we are primarily interested in the crystallographic structure, the data are presented as a function of $d=2\pi/Q$, where d corresponds to the spacing between interatomic planes.

The zeolite used was commercially available Linde 13X.[16] This zeolite consists of an alumino-silicate backbone with a face-centered-cubic crystal structure and a 25-Å unit cell.[17,18] The zeolite structure consists of 12-Å-diam pores connected by 9-Å-diam channels. The zeolite was outgassed in vacuum for 48 h at 380 °C and then loaded, under vacuum, in a cylindrical vanadium sample cell (1.27 cm diameter by 6.4 cm long). The cell was attached to the pot of a ^{3}He refrigerator, and diode thermometers at the top and bottom of the cell were used to monitor the temperature. The temperature of the two thermometers was within 0.5 K for all the measurements reported here.

The deuterium samples were prepared by heating the cell to 25 K, well above the liquid-solid transition for the bulk, and condensing fixed amounts of gas into the cell. The samples were then slowly cooled, over a matter of hours, to the temperature of the measurements. The samples were allowed to equilibrate for at least 1 h at each of the temperatures measured.

III. RESULTS

The scattering from the empty zeolite, before the adsorbtion of any D_2, was measured at 5.5 K and is shown in Fig. 1. The diffraction pattern consists of a multitude of peaks characteristic of the zeolite structure. These peaks can all be indexed within the known face-centered-cubic (fcc) structure of NaX-type zeolites[18] such as 13X zeolite. The unit-cell size determined via Rietveld refinement[19–22] was 25 Å, in good agreement with other members of this family.[17,18] A more complete description of the zeolite 13X structure will be published separately.[23]

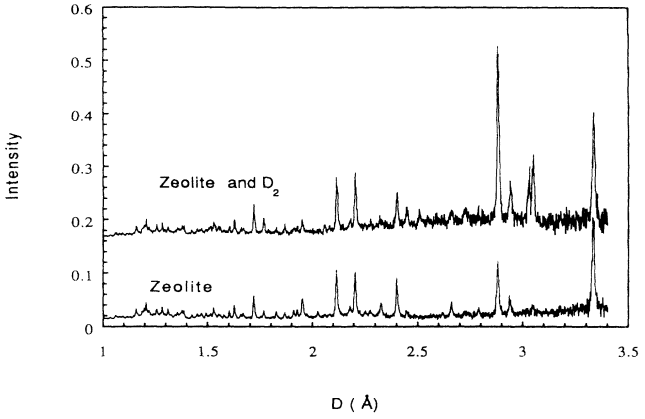

FIG. 1. (a) Scattering from zeolite 13X at 5.5 K. (b) Scattering from zeolite with 0.893 ℓ atm of adsorbed D_2 at 5.5 K.

A significant change in the scattering is observed when D_2 is adsorbed into zeolite. Figure 1 also shows the scattering at 5.5 K from 13X zeolite with 0.893 ℓatm of D_2 gas adsorbed. The addition of D_2 changes the intensity of some of the existing peaks and leads to the appearance of several new peaks. These changes in the scattering are due both to correlations among the adsorbed D_2 molecules and to correlations between D_2 and the atoms in the zeolite structure. However, none of the peaks from the zeolite structure are reduced in intensity or changed in position. This implies that D_2 simply adsorbs in the pore and channel structure of zeolite without causing any distortion or structural changes in the zeolite backbone. Thus zeolite can be treated as a fixed structure into which D_2 is simply adsorbed.

The additional scattering that appears on the adsorbtion of D_2 can be more easily observed if the fixed background due to zeolite is removed. This subtraction, using the observed scattering scaled by the incident beam intensity, is shown in Fig. 2. The small amounts of D_2 adsorbed in the sample do not significantly change the sample self-shielding, and no corrections for this effect have been included. This additional scattering will be referred to hereafter as the D_2 scattering.

The D_2 scattering consists of two components: sharp diffraction peaks and a broad background. The diffraction peaks indicate that the adsorbed D_2 has long-range translational correlations. The width of the diffraction peaks is limited by the instrumental resolution. This corresponds, for the PHOENIX spectrometer, to a correlation length or crystallite size on the order of 1000–1500 Å. Thus the correlations of the D_2 molecules are maintained at least over this distance scale.

The observed diffraction peaks for the absorbed D_2 are consistent with the fcc structure of zeolite.[17,18] The bars in Fig. 2 indicate the positions of allowed reflections

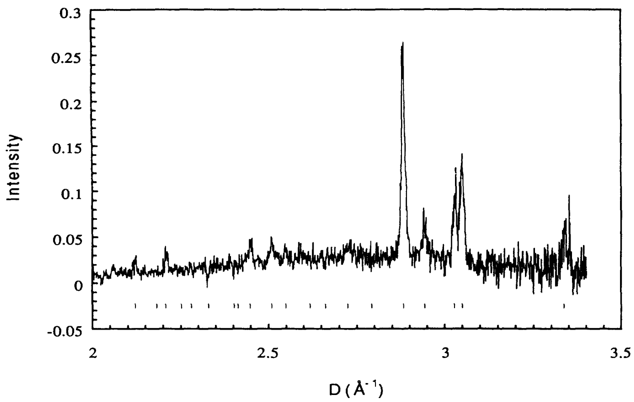

FIG. 2. Scattering from 0.893 ℓ atm of adsorbed D_2 with the empty zeolite scattering removed. The solid bars indicate positions of allowed reflections within the fcc structure of zeolite.

within the fcc structure of zeolite 13*X*. Note that not all reflections are present in either the zeolite or D_2-zeolite samples. This is due to phase cancellations between the scattering atoms within the unit cell. The particular arrangement of atoms in the unit cell determines the intensities of the reflections. It is important to note that the *d* values indicated are the only positions where reflections can occur within the fcc structure.

Within the accuracy of the measurement, all the peaks from the adsorbed D_2 can be indexed within this fcc structure. The peaks cannot, however, be indexed using any of the known structures for bulk solid D_2. This indicates that the D_2 molecules are simply binding to specific adsorbtion sites on the zeolite backbone and that no bulk solid D_2 is formed within the pores. The long correlation length is consistent with bound molecules since zeolite itself also has a long correlation length. Alternately, it would be surprising for a solid confined in the small pores of zeolite to have such a long correlation length. We have not, at present, identified the particular adsorbtion sites for D_2 in the zeolite structure. A full structural determination of the D_2-zeolite system via Reitveld refinement is under way and will be published separately.[23]

A broad structureless scattering is also present when D_2 is adsorbed into zeolite. This scattering is very broad and featureless and has two possible origins. One possibility is that this scattering is due to the short-range correlations of a liquid phase adsorbed in the pores. We view this as unlikely since the scattering does not show the characteristic short-range correlations expected for a liquid. In addition, as discussed below, this broad component changes very little with temperature, even well above the bulk liquid-solid transition. The alternate origin of the broad scattering, which we view as the most likely, is diffuse scattering.[24] This diffuse scattering could arise from several causes such as randomly occupied adsorbtion sites, large zero-point motion of the adsorbed molecules, or orientational disorder of the adsorbed molecules. These various possibilities cannot be distinguished in these studies.

The temperature dependence of the D_2 scattering is shown in Fig. 3. The scattering changes little with temperature from 5.5 to 24 K, well above the bulk liquid-solid transition temperature of 18 K.[3] The small temperature dependence observed, in particular the heights of the peaks at 3.05 and 3.34 Å, is not statistically significant. There is certainly no evidence of a transition from the low-temperature phase, where the molecules are adsorbed on the zeolite framework with long-range correlations, to a liquid. Such a transition involves the loss of long-range translational correlations and would be characterized by the disappearance of the diffraction peaks. No transition corresponding to the supercooled liquid-solid transition observed by Rall, Brison, and Sullivan[5] for H_2 is observed.

We have also carried out measurements for different amounts of D_2 adsorbed in zeolite. Figure 4 shows the temperature dependence of the scattering for a sample with 1.771 ℓ atm of D_2 adsorbed in zeolite. The behavior of the scattering in this case is different from the previous sample in that several of the diffraction peaks exhibit marked temperature dependence. In addition, these peaks are at different positions than in the lower filling sample. Several peaks also exhibit no temperature dependence, as in the lower filling sample. These temperature-independent peaks are located at the same positions as in the lower filling sample.

The temperature-independent peaks we interpret as D_2 molecules bound to strong adsorbtion site within the zeolite cage structure, as in the lower filling case. These peaks, which are located at 2.88, 3.03, 3.05, and 3.34 Å, are at the same location as in the lower filling sample and exhibit no variation with temperature between 5.5 and 24 K. This implies that the molecules in these adsorbtion sites are strongly bound and are not affected by the presence of additional D_2.

The temperature-dependent peaks we interpret as bulk D_2 either on the surface of the zeolite powder or in the spaces between the grains. These peaks, which are locat-

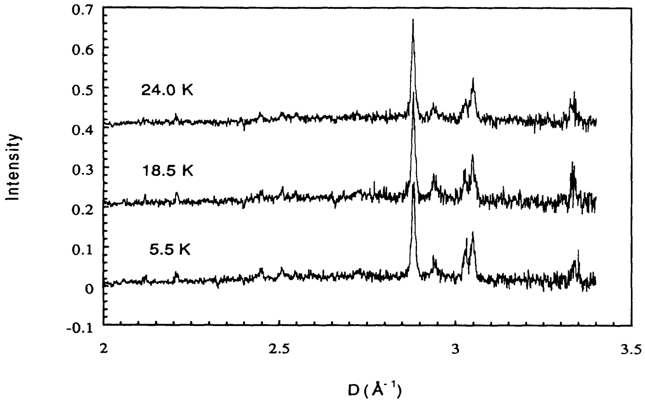

FIG. 3. Scattering from 0.893 ℓ atm of D_2 at temperatures of 5.5 K (bottom), 18.5 K (middle), and 24 K (top). The curves have been offset for clarity.

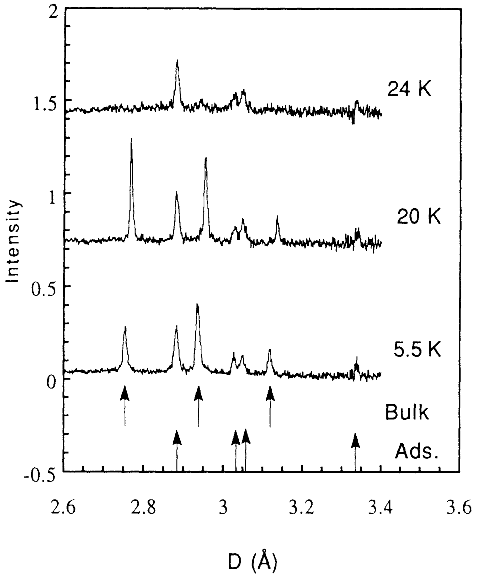

FIG. 4. Scattering from 1.771 ℓ atm of D_2 adsorbed in or on zeolite at temperatures of 5.5 K (bottom), 20 K (middle), and 24 K (top). The curves have been offset for clarity. The arrows at the bottom show the location of diffraction peaks for solid D_2 ("Bulk") and for D_2 adsorbed in zeolite ("Ads.") as determined from the 0.893 ℓ atm measurements.

ed at 2.76, 2.94, and 3.13 Å, agree well with the known hexagonal structure of D_2 in this temperature range.[25] The width of the peaks is dominated by the instrumental resolution, indicating that the D_2 crystallites responsible for the scattering are larger than 1000–1500 Å and are more likely located outside the zeolite cavities.

The peaks from bulk D_2 disappear between 20 and 22 K, which is in reasonable agreement with, but slightly higher than, the accepted value for the bulk liquid-solid transition for D_2.[3] This discrepancy is somewhat larger than the calibration accuracy of our thermometry (±1 K). It is not clear whether the discrepancy in the transition temperature is due to temperature uncertainties or to a physical effect due to adsorption of bulk D_2 onto the zeolite outer surfaces.

The diffraction peaks associated with bulk D_2 decrease in size as the filling is lowered and disappear completely between fillings of 1.252 and 1.264 ℓ atm as shown in Fig. 5. This filling is consistent with estimates of the zeolite pore capacity based on the atomic size of D_2 and the sample volume. The complete disappearance of the peaks for fillings of 1.252 ℓ atm and below lends support to the model where the pores fill first and, once the pores are filled, bulk D_2 forms in the intergrain voids.

The behavior of the adsorbed D_2 as a function of filling shows interesting behavior. At low filling the primary peaks appearing on the adsorbtion of D_2 are located at 2.88, 2.94 (weak), 3.05, and 3.34 Å. These peaks have been labeled $S1$ in Fig. 5. The location of these peaks are consistent with the fcc zeolite structure, indicating that they are D_2 molecules in well-defined adsorbtion sites in the zeolite structure. Their intensity is shown in Fig. 6. Two of the peaks, at 3.05 and 3.33 Å, do not change in intensity once the filling is above 0.705 ℓ atm, while the remaining peaks increase with increasing intensity.

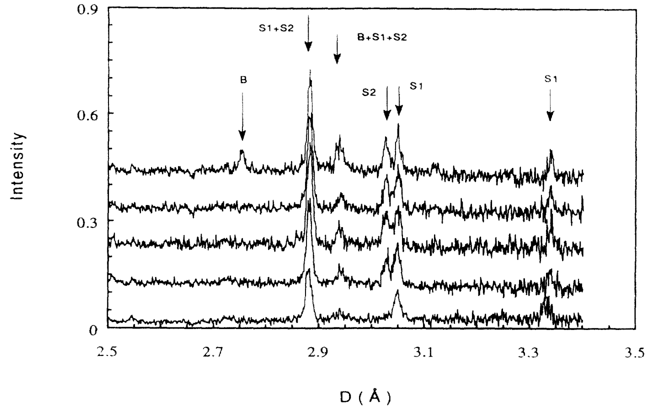

FIG. 5. Scattering from D_2 in zeolite at 5.5 K at a variety of D_2 fillings. The curves correspond, from bottom to top, to fillings of 0.705, 0.893, 1.024, 1.252, and 1.264 ℓ atm. The curves have been offset for clarity. The arrows indicate the location of reflections associated with the bulk and with adsorbtion sites $S1$ and $S2$, as described in the text.

Increasing the filling leads to an increase in the intensity of the peaks at 2.88 and 2.94 Å. In addition, a new peak appears at 3.03 Å. The location of this peak is still consistent with the fcc zeolite structure, indicating that it also arises from molecules in well-defined adsorbtion sites in the zeolite structure. Finally, upon further filling, bulk peaks appear and no further change in the intensity of the peaks associated with adsorbtion sites occurs.

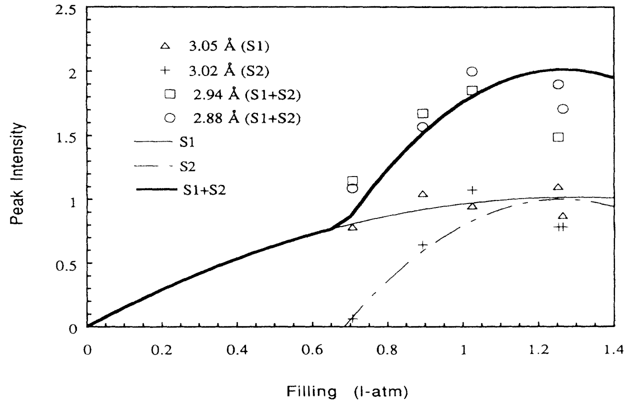

FIG. 6. Integrated intensity of the diffraction peaks as a function of D_2 filling. The peak intensities for each value of d have been scaled. The 3.05-Å ($S1$) and 3.02-Å ($S2$) peaks have been scaled so that they are approximately unity at a filling of 1.26 ℓ atm (full pore). The peaks at 2.94 Å ($S1+S2$) and 2.88 Å ($S1+S2$) have been scaled so that they are approximately 2 at a filling of 1.26 ℓ atm. The curves are simply a guide to the eye and sketch a realistic behavior of the $S1$ and $S2$ sites. The heavy line is simply the sum of the curves for $S1$ and $S2$.

The above results lead to a simple model for adsorbtion of D_2 in zeolite. At low fillings, D_2 is adsorbed into one particular adsorbtion site, which we designate $S1$. As the filling is increased, all molecules preferentially adsorb into these adsorbtion sites. Once these sites are saturated, which is indicated by the constant intensity of the diffraction peaks associated with the $S1$ sites, a second set of sites, labeled $S2$, begins filing. As the filling is increased, D_2 is adsorbed at $S2$ sites until they saturate. Once both the $S1$ and $S2$ sites are saturated, bulk D_2 begins to form outside the zeolite pore structure with no further change to the molecules adsorbed within zeolite.

Figure 6, which shows the intensities of the diffraction peaks as a function of filling, illustrates this behavior. At low fillings only the $S1$ sites are occupied and only the diffraction peaks associated with these sites have nonzero intensity. The form of the peak intensity, as a function of filling, has not been determined in these measurements. However, it is safe to assume that it is some monotomically increasing function of filling, as illustrated by the solid curve in Fig. 6. Once the $S1$ sites are saturated, the $S2$ sites begin to fill. The intensity of the diffraction peaks associated with the $S2$ sites then increases with filling, as illustrated by the dashed curve. Finally, once the $S1$ and $S2$ sites are filled, bulk D_2 begins to form outside the zeolite pore space.

We have attempted to obtain some measure of the binding energies of the two adsorption sites by studying the population of these sites at high temperatures. Unfortunately, our cell could not withstand sufficient pressure to allow us to do this at constant filling. Therefore we carried out a series of measurements at nonconstant filling between 5 and 80 K. The initial filling of 1.024 ℓ atm, at 5.5 K, was reduced to 0.867 ℓ atm, at 80 K, to limit the pressure in the cell to manageable values. However, this lower filling, at high temperatures, is still above the value where the $S2$ sites are occupied at low temperatures.

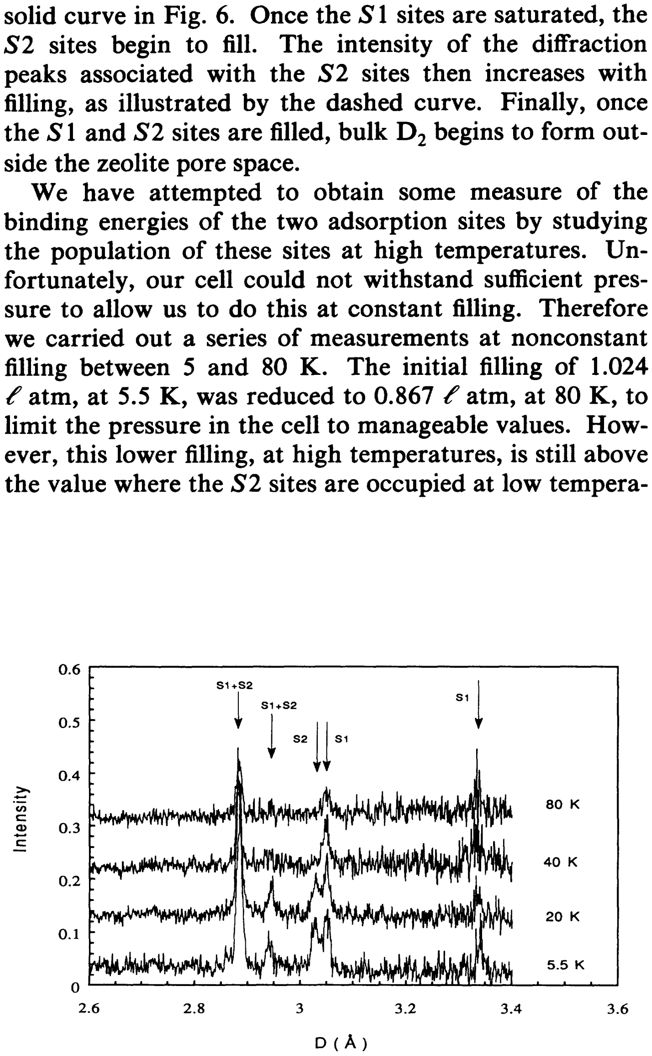

FIG. 7. Observed scattering at temperatures of 5.5, 20, 40, and 80 K. Note that the reflections associated with the $S2$ peak disappear at ~40 K. The reflections associated with the $S1$ peak are still present at 80 K.

The results of these measurements are shown in Fig. 7. At low temperatures diffraction peaks due to molecules in both the $S1$ and $S2$ sites are present. There is little change on raising the temperature to 20 K. Upon warming to 40 K, the peaks we associate with the $S2$ sites have almost completely disappeared. This indicates that the binding energy of these sites is on the order of 30–40 K. Note, however, that the peaks due to molecules in the $S1$ site show little change in intensity. Warming to 80 K reduces the intensity of the peaks, but they do not disappear completely. This indicates that the $S1$ sites are very strongly bound with an adsorbtion energy on the order of 80 K or higher.

IV. CONCLUSIONS

We have studied the microscopic structure, using neutron diffraction, of D_2 adsorbed in the pores and channels of zeolite $13X$ over a wide range of fillings and temperatures. The diffraction measurements indicate that D_2 adsorbs into the pores in well-defined adsorbtion sites on the zeolite. D_2, in a sense, becomes an integral part of the zeolite structure at low temperatures. Thus it is not appropriate to view D_2 in the zeolite pores as either a bulk liquid or a solid. Its structure and correlations are dominated entirely by the zeolite.

It is not surprising that no bulklike liquid-solid transition is observed for D_2 in the pores since the dominant interaction is between the zeolite backbone and D_2. We expect that the situation for H_2 will be comparable since the binding energies of H_2 and D_2 molecules are similar. The larger zero-point energy of H_2 in zeolite, as compared to D_2, might make H_2 more mobile. However, this additional zero-point energy is, when compared to the binding energies, probably not sufficient to change the results drastically.

In light of these results, the measurements of Rall, Brison, and Sullivan[5] which report a liquid-solid transition suppressed by finite-size effects, are somewhat surprising. Their conclusions, however, were based on NMR spin-spin relaxation measurements. These measurements are quite sensitive to changes in the correlation time of the molecules.[26] Unfortunately, they are not very sensitive to the origin of these changes in the correlation time. Thus, in the absence of a liquid-solid transition, as shown by this work, the transition observed by Rall, Brison, and Sullivan is most likely an orientational transition of the adsorbed H_2 molecules. We cannot, at present, extract information on the orientational correlations, either static or dynamic, of the adsorbed molecules. However, if the molecules are adsorbed in sites with only a weak orientation component, then it is possible that Rall, Brison, and Sullivan simply observed the decrease in the orientational correlation time of individual molecules bound in adsorbtion site in the zeolite structure.

We have identified two distinct binding sites, designated $S1$ and $S2$, for D_2 molecules within the zeolite pore network. These sites have large binding energies, > 80 K for $S1$ and ~40 K for $S2$, leading to the D_2 molecules being tightly bound to the D_2 structure. It is interesting to note that even though filling was carried out at 25 K, much lower than the absorbtion energy for either site, the $S1$ site always filled first. No filing of the $S2$ site, until the $S1$ sites were saturated, was observed. Given the low filling temperature, we would expect that molecules would simply become adsorbed in the first binding site they encountered. Absence of this behavior implies that the D_2 molecules may have an enhanced surface diffusivity, allowing them to sample various sites until they locate the lowest-energy configuration.

ACKNOWLEDGMENTS

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