

Supercooling of molecular hydrogen in zeolite

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Studies of the nuclear spin echoes and spin-spin relaxation times T_2 of hydrogen constrained to the interior of the molecular cages of zeolite have shown that liquid hydrogen can be supercooled well below the limits previously reported. The T_2 values peak sharply at the liquid-solid transition temperatures which have a strong, hitherto unobserved orthohydrogen-concentration and sample dependence. A similar behavior in T_2 has been observed for an HD sample which has no orientational degrees of freedom.

I. INTRODUCTION

There is considerable general interest in studying the properties of the condensed phases of hydrogen in restricted geometries. This interest is twofold. Firstly, solid hydrogen is a quantum solid for which both the translational *and* the rotational degrees of freedom must be treated quantum mechanically, and this results in unusual ordered structures and in quantum diffusion at low temperatures which will be modified dramatically in constrained geometries.^{1,2} Secondly, there is the possibility of observing new superfluid phases if molecular hydrogen can be cooled to sufficiently low temperatures.³

The isotropic intermolecular interactions which determine the molecular positions in the lattice are weak, the molecular masses are low, and the molecules are weakly localized with respect to the quantum-mechanical zero-point motion. The orientational degrees of freedom are those of quantum rotors for which the orbital angular momentum J is a good quantum number; $J=0$ for the para molecular species at low temperatures, and $J=1$ for the ortho species. In the bulk solid, the ortho species form orientationally ordered structures at low temperatures¹ if the ortho concentration is above 55%. This ordering is driven by the anisotropic interactions between the $J=1$ molecules. Below 55%, a quadrupolar glass state with a broad distribution of tensorial order parameters is observed at low temperatures.² We have carried out NMR investigations of the behavior of solid ortho-para mixtures in zeolite to explore the nature of the orientational ordering of a small assembly of quantum rotors ($N \sim 20$) with highly frustrated interactions. This is expected to be significantly different to the bulk behavior.

We were also interested in studying the supercooling of H_2 in restricted geometries following the pioneering studies of H_2 in vycor.⁴ Supercooling has been observed down to 10.6 K for small droplets,⁵ and down to 9.9 K for H_2 in vycor pores.⁴ The interest in supercooling is that molecular H_2 is one of the few systems other than 4He which offers the possibility of realizing a Bose condensation to a superfluid state.³ Para- H_2 is a spin-0 boson and would form a Bose-Einstein condensate at 6.7 K, neglecting interactions. Ortho- H_2 as a spin-1 boson has

no known counterpart and could form another anisotropic magnetic superfluid near 1 K.

The use of zeolite for studying supercooling is a natural extension of the earlier efforts using vycor. Supercooling in small pores of diameter D results from the suppression of solidification due to interfacial tension at the pore boundary. $T_{sc} = T_{melt}^{3D} - A/D$, and significant additional supercooling is expected for zeolite with $D \approx 9-12 \text{ \AA}$ compared to vycor with $D \approx 70 \text{ \AA}$.

II. EXPERIMENTAL PROCEDURE

We have used NMR techniques to investigate hydrogen in zeolite. Two different methods were employed. Continuous wave spectroscopy was used to observe the evolution of the quasistatic orientational order parameters which determine the line shapes at low temperatures.² The molecular dynamics were probed using pulse NMR techniques. Nuclear spin-spin (T_2) and nuclear spin-lattice (T_1) relaxation times have been measured to determine the spectral densities of the motion at low frequencies and high frequencies, respectively. "Ordinary" $90_x^\circ - \tau - 180_x^\circ$ spin-echo techniques were used to monitor the liquid fraction of the hydrogen sample directly. The dipolar broadened lines from the solid component of the sample do not contribute to the ordinary echo, and the echo amplitude, after correction for the T_2 decay, provides a reliable measure of the liquid fraction. rf amplitudes of 15 G were used at 268 MHz (for high sensitivity) and the spectrometer recovery time was 35 μsec .

The existence of the two species, ortho and para, results from the quantum mechanical requirement that the molecular wave function be totally antisymmetric for the two spin- $\frac{1}{2}$ nuclei (protons). For para- H_2 , the orbital function is even ($J=0, 2, \dots$) and the nuclear spin function odd ($I=0$). Ortho- H_2 has odd orbital symmetry ($J=1, 3, \dots$) and even nuclear symmetry ($I=1$), and is the only species observed by NMR. At high temperatures the ortho:para ratio is 3:1 (corresponding to the spin degeneracy), and in samples prepared from room temperature gas there is a slow ortho \rightarrow para conversion driven by the weak magnetic intermolecular interactions which can break the orbital and nuclear spin symmetries

simultaneously. The weakness of these interactions allows us to study ortho- H_2 in a metastable form over a long period of time. The ortho concentration x is monitored by measuring the cw NMR absorption line shape whose integral is directly proportional to x at a given temperature. The temperatures were measured using a calibrated carbon-glass thermometer. We have observed a strikingly unusual ortho-para conversion in zeolite with a slow conversion of $0.43\% \text{ h}^{-1}$ at early times ($t < 500 \text{ h}$) followed by a *faster* conversion at later times at $2.2\% \text{ h}^{-1}$. This will be discussed in detail elsewhere.

A Kel-F NMR sample cell (3 mm I.D., 3 mm length) was filled with commercially available zeolite.⁶ Zeolite 13X is an aluminosilicate with the chemical formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \times \text{H}_2\text{O}$. Its structure is complicated but regular and contains pores (12 Å) and connecting channels (9 Å). The fundamental building block is an oxygen tetrahedron with a centered Al or Si atom. Eight tetrahedra form a cube. These assemble corner to corner and leave open spaces in between. The zeolite was out-gassed for 10 h at 600°C and 10^{-5} Torr, and then loaded into the cell immersed by a dry N_2 atmosphere to prevent O_2 and H_2O from reabsorbing onto the clean surfaces. The cell was sealed by heating the Kel-F and consequent heat shrinking onto brass endcaps.

III. OBSERVATIONS AND INTERPRETATION

The hydrogen sample was prepared by heating the cell to above 15 K and condensing fixed amounts of gaseous hydrogen through a heated sample line into the sample cell. The sample was annealed for about half an hour at 14 K and then cooled to 4.2 K within 1–15 h. Supercooling was observed directly by monitoring the ordinary spin-echo amplitudes. During cooling the recorded

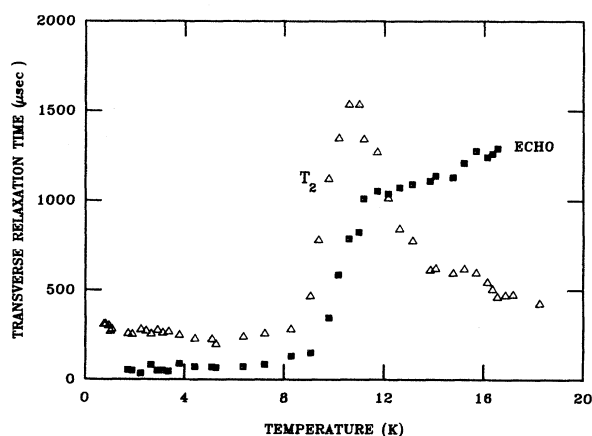


FIG. 1. Temperature dependence for the nuclear spin-spin relaxation time (T_2) of H_2 in zeolite for an ortho concentration $x=0.73$ (open triangles). The temperature variation of the echo amplitudes, corrected for the $1/T$ dependence and the T_2 decay, are shown by the solid squares for this sample ($x=0.73$). The peak in T_2 corresponds to the temperature of solidification of the supercooled liquid.

NMR echo heights increased steeply around 11 K forming a distinct peak at about 10 K and then dropped sharply by a factor of 20. The latter change is attributed to the liquid-solid transition. The initial change in echo heights is due to the occurrence of a dramatic peaking of the nuclear spin-spin relaxation time T_2 . The behavior for both the echo amplitudes and T_2 is shown in Figs. 1 and 2 for two different samples. The echo amplitudes in Fig. 1 have been extrapolated back to “zero” time to correct for T_2 decay reductions. This correction was not made for the data of Fig. 2 because the T_2 and echo measurements were taken at different times and therefore for different ortho concentration, hence the shift in the peaks of the two sets of data. The products of the echo amplitudes and the temperature (to correct for Curie law) shown in Figs. 1 and 2 are proportional to the liquid component. The average relaxation time is shown in Figs. 1 and 2 for the two samples, but two components (at short times and long times) can be distinguished and are attributed to the narrow and broad components of the NMR line shape, respectively. Although the general features are the same for different samples the shape of this transition varies.

The supercooling temperature T_{sc} (for the echo height) falls in the range 8.5 to 12.5 K, depending on sample preparation and history. The width and relative heights of the transition are equally sample dependent. Two effects are observed. Firstly, the sharpness of the peak decreases as the cooling time increases between 15 and 4 K. The peak becomes broader and the relative height decreases. A weak connection seems to exist between a longer cooling time and higher T_{sc} . Slower cooling allows the sample to form more homogeneously which leads to a less suppressed solidification. Secondly, the

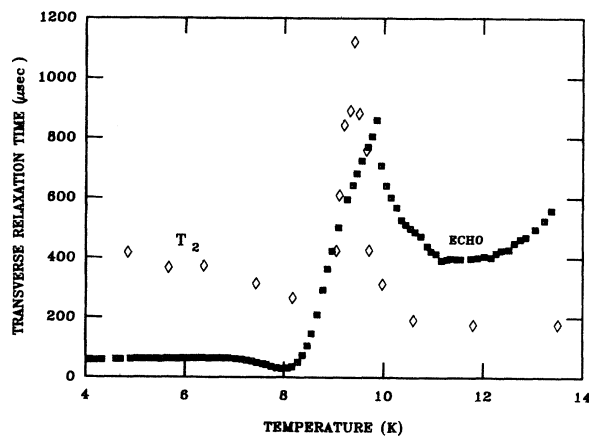


FIG. 2. Temperature dependence for the nuclear spin-spin relaxation time (T_2) of H_2 in zeolite for an ortho concentration $x=0.63$ (open diamonds). The temperature variation of the ordinary echo amplitudes (corrected for the $1/T$ dependence) for this sample is given by the solid squares for $x=0.74$. (x is larger because the echoes were measured before the T_2 values, and the T_2 correction could not be made to the echo measurements.) As in Fig. 1, the peak in T_2 signals the solidification of the supercooled liquid at T_{sc} .

sample preparation, temperature and pressure of condensation, and the filling of the pores are never precisely reproducible.

An important result of these studies is the ortho concentration dependence of the supercooling transition temperatures T_{sc} . The T_{sc} could be fit to a linear function of the para- H_2 concentration (Fig. 3). This has not been observed in previous studies and is interesting because it indicates that supercooling is easier to achieve for para- H_2 (the spherically symmetric species). This is expected because of the additional orbital degeneracy and the anisotropic interactions of the ortho- H_2 molecules. The T_{sc} inferred from the T_2 studies extrapolates to 13.4 ± 0.5 K at zero para concentration, and 3.3 ± 0.8 K for zero ortho content with a slope of -0.10 ± 0.01 K%.¹ The values of T_{sc} for low ortho contents are especially interesting because they are within the range of the predicted superfluid transitions. This region, however, could not be probed using NMR because of the weakness of the NMR signals for very low ortho concentration.

It has been established that the T_2 transition peaks are nonhysteretic, by thermally cycling through the peaks. We therefore deduce that this supercooling is purely thermodynamic, and is very different to the dynamical supercooling observed by other groups for larger geometries.^{2,7,8} The sharpness of the T_2 peak and the value of T_{sc} are, however, dependent on the sample preparation. The T_1 data did not show any evidence for a transition over the temperature range $3 < T < 18$ K.

cw line shapes were recorded in order to evaluate the quasistatic orientational order parameter. The orientational ordering of a small number of quantum rotors with highly frustrated interactions raises a number of questions concerning the nature of the phase transitions and type of order achieved. For axial quadrupoles the order parameter is given by $\sigma = \frac{1}{2} \langle 3J_z^2 - J^2 \rangle$.^{2,9} A single crystal sample would result in two NMR absorption lines at $\omega_L \pm \Delta\omega(\theta, \sigma)$ with θ the angle between magnetic field

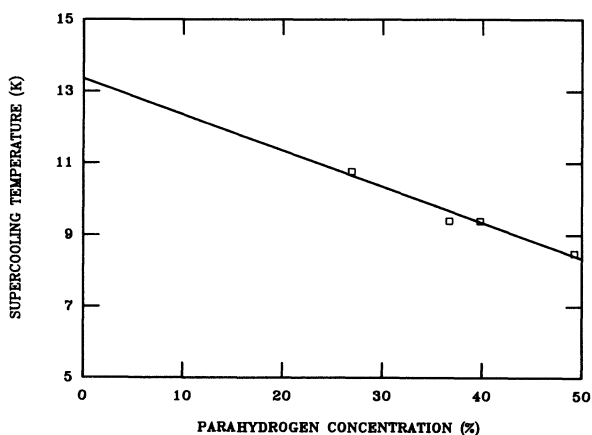


FIG. 3. Dependence of the supercooling transition T_{sc} on the para- H_2 concentration. The intercept for pure ortho- H_2 is 13.4 ± 0.5 K.

and the local molecular symmetry axis, ω_L being the Larmor frequency. For a powder sample this leads to a Pake doublet with sharp features. If in addition σ is not a fixed value, the line shape becomes a smooth bell shape.² For the line shapes observed at 4 K we find that there are two components: (a) a relatively narrow central (liquid-like) component corresponding to approximately 20% of the spins, and (b) a broad line (~ 140 kHz in width) which we associate with a broad distribution of Pake doublets. From a computer simulation for the Pake doublet superposition we deduce that the order parameters σ have a distribution around a mean of about 0.5 with a width ~ 0.4 . In this analysis we found that the outer wings of the Pake doublet superposition were below noise levels and not observable. The interpretation of this cw NMR result is that at least a certain percentage of ortho molecules are partially ordered as small clusters. The roughness and inhomogeneity of the zeolite surface would be expected to lead to such a distribution of σ for partially ordered states. This analysis will be discussed in detail elsewhere.

The cw line shapes evolve smoothly from 4.2 to 15.8 K. The initially dominant center component decreases in weight with increasing temperature. For high temperatures only the broad contribution remains. No sharp transition around 10 K can be seen and the change in the nature of the line shape implies that on warming one contribution of the H_2 sample leaves the cell first. We attribute the overall temperature behavior to the existence of a two-component system: (1) molecules on the surface with $\sigma \approx 0.5$, partially ordered in clusters with a relatively broad distribution of order parameters, and (2) a bulk disordered contribution with $\sigma \approx 0$ in the center of the pores. This two-component model is consistent with both the T_1 and spin-echo measurements. The observation that the T_1 data do not show evidence of a phase transition supports the interpretation of the peak in T_2 and the spin-echo amplitudes in terms of the solidification of the liquid component rather than an abrupt change in the spectral density of the system.

We have carried out additional studies using zeolite with smaller dimensions to determine the relative significance of the wall behavior. The supercooling transitions observed for H_2 in zeolite 5A (5 Å channels, ~ 8 Å pores) are much sharper. T_2 drops from 2 msec above 11 K to values < 10 μ sec, which is shorter than the recovery of the spectrometer, and echoes cannot be observed. The cw NMR line shapes also differ. In contrast to zeolite 13X, almost no wing contribution is observed. The width at half height is unchanged (16 kHz) but the line is only 60 kHz wide instead of 140 kHz. This confirms the view that complete orientational ordering is not observed in very small clusters ($N < 15$). The line shape broadens upon cooling from 4.2 to 1.6 K by a factor of 1.5 indicating a higher degree of ordering. The picture, that arises from the width of the resonance line, is that the cluster size decreases with the reduction in available space.

IV. CONCLUSION

The data obtained point toward a supercooling transition with an associated partial orientational ordering on

the surface walls. Two more crucial tests were performed. Firstly, we tested for an orientational ordering transition below 4.2 K. The line shape broadened from 130 kHz at 4.2 K to 200 kHz at 0.95 K. But more importantly, the weight of the line shifted towards the wings, indicating additional orientational ordering. Secondly, the same echo height and T_2 measurements were carried out for hydrogen deuteride (HD). HD is spherically symmetric in its ground state, has no electric-quadrupole moment, and orientational ordering is impossible. Both data sets are not as distinct as for H_2 but they do show the same supercooling features at about 10 ± 0.1 K. This further supports the interpretation of the results in terms of supercooling by more than 5 K for hydrogen in zeolite.

Further theoretical work is needed to understand the apparent partial orientational ordering of orthohydrogen in restricted geometries, and the related dependence of the supercooling transitions on ortho concentration. The latter is especially important for exploring the temperature range where superfluidity has been predicted.

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