Properties of Immobile Hydrogen Confined in Microporous Carbon

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Abstract

We report [results of vibrational](#) neutron [spectroscopy](#) investigation aimed to identify the state of hydrogen adsorbed in ultramicroporous carbon. The mobility of hydrogen confined in carbon pores was probed as a function of temperature and pressure using inelastic neutron scattering, and the molecular translational and rotational motions were studied. At low loading rotation of H₂ molecules adsorbed in the smallest carbon pores (~4–5 Å) is severely hindered, suggesting that the interaction between H₂ and the host matrix is anisotropic. At higher loading, H₂ molecules behave as a nearly free rotor, implying lower anisotropic interactions with adsorption sites. At 77 K where bulk H₂ is a gas, deconvolution of elastic/quasielastic signal provide evidence of pressure-dependent fractions of immobile (solid-like) and partially mobile (liquid-like) hydrogen, which correlate with the excess adsorption isotherm at 77 K. Effective H₂ density in pores changes from solid-like to liquid-like with increasing pressure at 77 K. Surprisingly, immobile and partially mobile H₂ is present even at temperatures as high as ~110 K where bulk hydrogen exists only in gas form.

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1. Introduction

Hydrogen storage remains the primary bottleneck to be overcome for the successful implementation of hydrogen-based technology in various applications, and is still a major challenge for materials science. In order to find better hydrogen storage materials, different porous materials have been discovered and studied over the years [1-5]. The results showed that the uptake of physisorbed hydrogen is closely connected to the available pore volume and surface area of porous materials. It was found that the presence of micropores (< 2 nm), and in particular ultramicropores (< 0.7 nm), is most desirable for hydrogen adsorption [6-14], in perfect agreement with theoretical modeling results [15,16]. Carbon materials are among the most investigated adsorbent materials [17] because of their low density, extensive pore structure, chemical stability, low cost, accessibility, and recyclability [18]. Electron microscopy results show that activated carbons consist of isotropic three dimensional networks of wrinkled atomic thin graphene sheets, and that the irregular stacking of crumpled sheets forms micropores of few Å in size [19,20]. The large variation in pore morphology results from differences in raw materials, carbonization, and activation methods [21,22]. Identifying strong adsorption sites and the adsorption mechanism in the microporous activated carbon is necessary to design better host materials for hydrogen storage.

This work presents a neutron vibrational spectroscopy investigation of molecular hydrogen confined in microporous carbon. Vibrational spectroscopy [23] is a well-known analytical technique that provides information on structure, bonding, and interactions in chemical systems, with the most popular examples being infrared (FTIR) and Raman spectroscopy techniques. Using neutrons in vibrational spectroscopy studies on hydrogen adsorption takes advantage of the particularly high sensitivity of neutron scattering by hydrogen species. The high penetration of neutrons in solid materials allows studies on adsorbed species and in-pore

confined molecular species as well. Moreover, neutron scattering instruments use a variety of sample environments, including in-situ gas adsorption from high vacuum to high pressures, and controlled temperatures from cryogenic to elevated temperatures. Depending on the type of neutron spectrometers it is possible to investigate a multitude of properties in the hydrogen / carbon system. By small-angle neutron scattering (SANS) [24,25] it has been found that the density of H₂ in micropores is about twenty times higher than the bulk gas at ~ 35 bar and room temperature [25]. Higher pressure (~ 200 bar) results obtained by SANS at room temperature showed that H₂ adsorbed in narrow micropores (< 9 Å) reaches the density of liquid hydrogen [24]. These experimental results are in line with empirical estimates according to which H₂ adsorbed in narrow micropores is in a highly dense state [26], most likely liquid [27]. Theoretical predictions for H₂ in narrow slit-shaped carbons led to the same result [28,29]. Challenging the view that the highest densification state of supercritical hydrogen in carbon micropores is the liquid state [9,27], a recent inelastic neutron scattering (INS) study provided direct evidence of solid-like hydrogen immobilized at 77 K at pressures as low as 0.2 bar [30]. Prompted by this result, the main purpose of this work is to further investigate the physical state of H₂ adsorbed in carbon pores using dynamic neutron scattering methods over a broader range of pressures and temperatures. The dynamics of adsorbed H₂ molecules as a function of thermodynamic parameters such as temperature and pressure reveals the nature of the interaction between H₂ and the host matrix, and provides insight into the actual physical state of adsorbed H₂. Recently, quasielastic neutron scattering (QENS) studies on the dynamics of H₂ and D₂ confined in carbon micropores showed that the diffusion onset temperature is higher for H₂ than for D₂ [31]. This observation, which is the opposite to what is predicted by classical physics, is the consequence of quantum behavior at cryogenic temperatures of H₂ and D₂ molecules restricted in the overlapping potential of pore walls in ultramicropores. The QENS study suggests that classical notions of liquid and solid

have different signification when applied to H_2 adsorbed in sub-nanometer sized pores [32]. It is important to note that the information on diffusive motion of adsorbed molecules provided by QENS technique is obtained from high resolution measurements ($\sim \mu\text{eV}$) of the scattering signal broadening near the elastic peak. It conveys information on both mobile and immobile species. However at higher temperatures it is difficult to determine both components if the instrument is a high resolution QENS spectrometer, since most of the diffusive behaviors will be outside the instrument measurement window. In an inelastic neutron scattering (INS) spectrometer it could be possible to determine the total contribution to the intensity due to both species, although the resolution is oftentimes not good enough to deconvolute the elastic and quasielastic contributions.

The main finding of this paper is the persistence of immobile (solid-like) and partially mobile (liquid-like) H_2 confined in carbon pores over a broad range of pressures and temperatures, including high pressure (up to 40 bar) and supercritical temperatures (up to 110 K). The nature of the interaction potential between H_2 and adsorption sites has been probed by monitoring the para $\rightarrow$ ortho transition as a function of temperature, pressure, and H_2 loading. In addition, a quasielastic analysis at low energy transfers was performed to the extent afforded by the spectrometer limitations. From the quasielastic signal broadening around the elastic line it was possible to estimate the proportion of immobile (solid-like) and partially mobile (liquid-like) species as a function of surface loading at 77 K. The results showed that the effective density of pore-confined H_2 at 77 K depends strongly on pressure and local pore width. This work demonstrates that the previous observation by one of the co-authors of immobile H_2 above its critical point [30] was not an isolated finding, but a part of a general behavior of in-pores confined H_2 . The significance of these findings reaches beyond the immediate interest in adsorption theory and confined fluids behavior, and is expected to infuse a new impetus into the search for the optimal hydrogen storage material.

2. Experimental

Ultramicroporous carbon (UMC) is a chemically activated porous carbon made available by MeadWestvaco Corporation (Charleston, SC) [33]. Gas adsorption characterization of surface properties [22] established that UMC has high surface area ($S_{BET} = 2450 \text{ m}^2/\text{g}$) and high total pore volume ($V_{tot} = 1.19 \text{ cm}^3/\text{g}$). The pore size distribution calculated from N_2 and CO_2 adsorption is presented in Figure S1 of Supporting Information. About 70 % of V_{tot} is contained in micropores ($< 20 \text{ \AA}$), and 20 % of V_{tot} comes from ultramicropores ($< 7 \text{ \AA}$). Quantitative analysis of SANS patterns recorded for the “dry” UMC material (in vacuum, before exposure to hydrogen) produced similar conclusions [34]. Hydrogen adsorption on UMC shows unusually high uptake capacity at 25°C (0.8 wt % at 20 bar) with slow kinetics and desorption hysteresis [22,25]. Adsorption of H_2 at 77 K reaches 5.5 wt % at 20 bar, which is comparable with the best known activated carbons (e.g. Maxsorb, AX-21) often referenced as standards for cryogenic H_2 physisorption. The excess adsorption data measured volumetrically (up to 1 bar) and gravimetrically (up to 20 bar) at 77 K are shown in Figure S2 of Supporting Information. High pressure adsorption data were fitted using with the Unilan isotherm, which is an extension of the Langmuir model for patch-like surfaces consisting of energetically uniform patches [35]. Using this model it was possible to extrapolate the adsorption isotherm at 77 K up to the highest pressure (40 bar) of current INS measurements. The Unilan parameters were used to estimate the H_2 loading, q_P , after exposure to various pressures (P) at 77 K. The corresponding relative surface coverage degree, θ_P , was calculated by normalizing to the asymptotic saturated adsorption amount ($q_s = 32.5 \text{ mmol/g}$) obtained from fitting the Unilan isotherm. Details are available in the Supporting Information file.

Inelastic neutron spectroscopy (INS) measurements were carried out on the VISION spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory. VISION is a particularly powerful neutron vibrational spectroscopy instrument, very similar to its optical counterparts – FTIR and Raman spectrometers – but with a remarkable sensitivity to hydrogen species in a very flexible sample environments. With a broad energy range extending from -3 up to 1000 meV (or 8065 cm^{-1}) VISION offers good resolution (0.10 meV around the elastic line and 1.2 % $\Delta E/E$ above 5 meV) in a range of momentum transfer vector Q (1.3 to 30 $\text{\AA}^{-1}$) that corresponds to physical lengths between 0.2 and 4.2 $\text{\AA}$ [36]. Thus, this instrument is optimized for high Q vibrational studies over broad energy ranges. The closest instrument of the same type is the TOSCA apparatus in UK. VISION measures the time of flight of each neutron for a fixed geometry configuration and integrates the signal within certain values of Q . Thus the Q vector information is not available in VISION, and generally it is not required for vibrational spectroscopy. Moreover, the distribution of all resolution components is not strictly Gaussian [36].

The UMC sample in powder form (0.5 g) was outgassed for ~20 hours at 300 °C (residual pressure < 0.1 Pa), sealed into a cylindrical Al can (6 mm diameter) and subsequently loaded into a closed cycle He refrigerator. The INS spectrum of “dry” UMC was acquired in the range of 5 to 77 K and was used for background subtraction. Figure 1 shows a schematic of experimental conditions employed in this work and their relationship with the phase diagram of bulk H_2 .

Figure 1: Experimental conditions in the three series of experiments (indicated by numbers) and their relationship with the phase diagram of bulk hydrogen [37].

Three series of experiments were performed. The first series comprised four runs at various sub-atmospheric pressures for studying the effect of temperature on hydrogen adsorbed at low surface coverage. These experiments used p-H₂ obtained by conversion of 99.9995 % purity normal hydrogen (n-H₂) over Cr₂O₃ catalyst at 20 K. The present set-up can provide up to 99.5 % of p-H₂. The p-H₂ was injected over the UMC sample at 77 K at fixed pressures (12, 52, 100 and 167 mbar) and allowed to equilibrate for one hour. Equilibration was accompanied by partial conversion to o-H₂ mediated by the paramagnetic centers present in UMC. The sample cell was then isolated, cooled down to 5 K, and the INS spectra were recorded temperatures in the range of 5–77 K. In the second series of experiments the effect

of n-H₂ pressure at 77 K was studied up to 40 bar. High purity n-H₂ was introduced to the sample at 77 K at various pressures and the sample pressure was kept constant during data acquisition by keeping the sample cell in contact with the gas reservoir. In a third series, the temperature effect on adsorbed n-H₂ was studied at a constant pressure of 3.25 bar and temperatures from 77 K to 150 K. The inelastic spectra of adsorbed H₂ were obtained by subtracting the spectrum of “dry” UMC from the spectra of hydrogen-loaded UMC.

3. Theoretical Background

Solid H₂ behaves as a three-dimensional quantum rotor with energy levels given by

$$E_J = BJ(J+1) \quad (1)$$

Here, J is the quantum rotational number ($J = 0, 1, \dots$), and B is the rotational constant of hydrogen defined as

$$B = \frac{\hbar^2}{2\mu d_e^2} = 7.35 \text{ meV} \quad (2)$$

where μ is the reduced mass of the molecule, and d_e is the equilibrium distance between the two protons (0.741 Å in the free state) [38]. The two nuclear-spin isomers of molecular H₂, namely ortho-hydrogen and para-hydrogen, differ by the parity of rotational quantum number, as required by the total wave function symmetry with respect to the permutation of the two nuclei. The states with even J values are called para-hydrogen (p-H₂) while those with odd J values are called ortho-hydrogen (o-H₂). The rotational states are spin-locked, meaning that isolated p-H₂ molecule cannot convert into o-H₂. The conversion is slow in gas phase, but readily happens in the presence of paramagnetic sites on surfaces, and in such case the relative population of both species is determined by temperature [39].

Neutrons have spin and their interaction with H_2 molecules (i.e., in the INS) can cause para ($J=0$) $\rightarrow$ ortho ($J=1$) transition. This transition is observed [40] in solid H_2 and for H_2 adsorbed on the surface of different materials, e.g. Grafoil [41]. In all these cases the transition takes place at an energy $2B = 14.7$ meV as expected for a 3-D free quantum rotor. Since the rotational energy of molecular H_2 is comparable with the adsorption energy of physisorbed hydrogen (about 30 meV per H_2 molecule) [42-44] the rotational motion is retained after physisorption, but its character is altered by the adsorption potential. In a weak isotropic potential, adsorbed H_2 continues to behave as a free rotor. If the potential is anisotropic the rotational symmetry is perturbed. If the adsorption potential anisotropy is small, the effect is a small shift of the rotational level and H_2 behaves as a nearly free rotor. In the presence of a large anisotropic potential, the degeneracy of the $J = 1$ state of H_2 molecule is lifted and the rotational line splits. This hindered rotational motion is frequently observed for H_2 adsorbed in microporous materials with pore sizes close to the molecular diameter [45,46]. As the anisotropic potential becomes infinitely large, the rotational motion tends to be confined in either the surface-normal or parallel direction, depending on the sign of anisotropic potential, leading to one-dimensional or two-dimensional rotation, respectively [47,48]. Thus, the $J=0 \rightarrow 1$ (para $\rightarrow$ ortho) rotational transition can be used as a probe of the interaction potential of H_2 with adsorption sites. INS is quite sensitive to the dynamics of molecular H_2 due to its large spin incoherent neutron cross-section, and in particular to the rotational transitions [49]. The INS technique has been widely used to probe the molecular hydrogen confined in the carbon-based porous materials including single-walled carbon nanotubes and nanohorns [45,46,50-57]. It has been shown in these studies that the presence of different adsorption sites for H_2 causes energy shifts of the rotational peak.

4. Results and Discussion

Figure 2 shows a typical inelastic spectrum of adsorbed H_2 at 25 K and 167 mbar loading. The energy transfer range is from -2 to 1000 meV. The cross-section for elastic neutron scattering from p- H_2 is negligible compared to that of o- H_2 (see Figure S3 of Supplementary Information) [58,59]. The occurrence of the elastic peak confirms that some fraction of p- H_2 delivered by the catalytic convertor was converted back into o- H_2 by the paramagnetic impurities in UMC. The zoomed spectrum in the inset shows the rotational peak at 14.6 meV corresponding to para $\rightarrow$ ortho transition. Broad recoil peaks are observed at higher energy transfer. The first recoil peak corresponds to recoiling molecules undergoing a rotational transition from $J=0$ to the $J=1$ states. The additional recoil peaks can be attributed to the recoiling molecule undergoing higher order rotational transitions. At high energy transfer the roto-vibrational spectrum of H_2 is superimposed over the recoil background [60].

Figure 2. Typical INS spectrum for adsorbed p- H_2 at 25 K corresponding to $P = 167$ mbar loading (6.7 mmol/g, $\theta_p = 0.21$). The zoomed view (inset) shows rotational and recoil peaks. $S(Q, w)$ is the dynamical structure factor in forward direction.

Only the elastic scattering and first rotational peak are analyzed here. The integrated intensity of the INS spectrum is proportional to the total amount of H_2 in the sample. Gas phase H_2 molecules do not scatter elastically (they just recoil) so their contribution to the total spectra is smeared along the whole energy range. Elastic scattering occurs only from immobile (solid-like) H_2 molecules, whereas partially mobile (liquid-like) H_2 contributes towards the quasielastic broadening at energy transfers near $E = 0$. The elastic and quasielastic scattering provide information on immobile and partially mobile o- H_2 primarily, as the elastic scattering cross-section of p- H_2 is quite small [59]. The recoilless rotational peak can only be observed for immobile solid-like H_2 molecules [40,41]. Thus, the integrated rotational peak area gives information on the immobile p- H_2 molecules. The shape and position of the rotational peak provides information about the interaction potential of the binding sites

4.1. Surface Potential at Very Low Initial Loading

Figure 3. Elastic and quasielastic scattering signal (a) and rotor peak (b) at $P = 12$ mbar loading (1.69 mmol/g ; $\theta_P = 0.05$) as a function of temperature. Inset in (a) shows data on the logarithmic scale. $S(Q, w)$ is the dynamical structure factor in forward direction.

The background and baseline subtracted elastic/quasielastic scattering signal and rotor peak corresponding to the lowest dosing of H₂ are shown in Figure 3. The method of baseline subtraction is shown in Figures S4 and S5 of Supplementary Information. At the lowest loading the quasielastic signal broadens with temperature. A strong splitting of the rotational peak is observed, indicating that rotational motion of low-dose adsorbed H₂ is strongly hindered. The free quantum rotor energy for para→ortho transition in solid hydrogen is 14.7 meV [40]. The degeneracy of the ortho state is lifted in the presence of a strong anisotropic potential. The $J = 1$ state is split into $m = \pm 1$ (rotation axis of molecule perpendicular to the adsorbed surface) and $m = 0$ (rotation axis of molecule parallel to the adsorbed surface) [47]. The magnitude of rotor peak splitting depends on the anisotropy of the potential. The rotor peaks were fitted using two Gaussians as shown in Figure S6 of the Supplementary Information. The peak energies are 13.4 (± 0.1) meV and 15.1 (± 0.1) meV. The ΔE_{rot} is calculated as 1.7 meV. Although peak intensity decreases with temperature, the peak positions and the magnitude of their splitting do not vary with temperature at this very low loading (1.69 mmol/g; $\theta_p = 0.05$) corresponding to $P = 12$ mbar exposure at 77 K.

The splitting of the rotational peak can be understood as follows: The adsorption potential $V(z, \theta)$ of a molecule is primarily characterized by its well depth and anisotropy, where z is the distance of the center of mass of the molecule from the surface and θ is the polar angle of the molecular axis with the surface normal [47]. The potential can be expressed as sum of Legendre functions, i.e., $V(z, \theta) = \sum_{l=0}^{\infty} V_l(z) P_l(\cos \theta)$. Since H₂ is a homonuclear molecule, l is restricted to even integers. For isotropic potential $V_0(z)$ the value of l becomes 0 and the adsorbed molecules behave as free rotors. Furthermore, rotational transition is expected to occur at 14.7 meV for H₂ adsorbed under an isotropic potential.

The anisotropic potential can be expressed as $V(z, \theta) = V_0(z) + V_2(z) P_2(\cos \theta)$, where the ratio V_2/V_0 defines the degree of anisotropy. For $V_2/V_0 \ll 1$, a slight shift of the rotational line is

observed. In this case, H_2 molecules behave as nearly free rotors. However, for $V_2/V_0 < 1$, the degeneracy of the $J = 1$ state is removed and splitting of rotational line occurs. In this case, H_2 molecules undergo hindered rotational motion. In order to estimate the rotational barrier, a double-well hindering adsorption potential of the form $V(z, \theta) = \frac{V_2}{2}(1 - \cos 2\theta)$ was assumed. The rotational constant B and the potential barrier V_2 for the lowest H_2 loading have been calculated using DAVE software [61]. The values found are $B = 7.27$ meV and $V_2 = 4.27$ meV, respectively. In fact the value of B determined here (7.27 instead of 7.35) can be attributed to the difference in the zero point energy between ortho- and para- hydrogen [62]. The strong anisotropic potential is located at low-symmetry sites, like surface steps and kinks. It was previously shown that wrinkling of the graphene sheet is driven by topological defects that are not well controlled during charring and activation of carbons [19]. The narrow spaces in micropores create a strongly anisotropic environment. The strongest adsorption energy sites, where adsorption occurs at very low loadings, are the narrowest pores with sub-nanometer size present in UMC. Here the overlapping potential from opposite pore walls enhances the confinement effect. The strong anisotropic potential experienced by H_2 molecules confined in micropores causes high density of the adsorbed H_2 as observed by SANS measurements [24].

4.2 Effect of Pressure and Temperature at Low Surface Loading

Figure 4. Elastic and quasielastic scattering signal (a) and rotor peak (b) at $P = 167$ mbar loading (6.73 mmol/g; $\theta_P = 0.21$) as a function of temperature.

The elastic/quasielastic scattering signal and rotor peak corresponding to exposure to $P = 167$ mbar at 77 K (6.73 mmol/g; $\theta_P = 0.21$) are shown in Figure 4. Compared to 12 mbar loading ($\theta_P = 0.05$) a much more significant broadening of the quasielastic signal with temperature is observed at 167 mbar loading ($\theta_P = 0.21$). This indicates that the mobility of adsorbed hydrogen is higher at this loading and that it has strong temperature dependence. It is important to recall that broadening of the quasielastic signal was much less pronounced at the lowest loading. This indicates that molecules occupy sites with relatively weaker adsorption potential as loading increases. It is also observed from Figure 4 that the rotor peak reduces to a single asymmetric peak at 14.6 meV, indicating nearly free quantum rotor behavior of H_2 . At this higher loading the strongest adsorption sites in narrow micropores are saturated, and adsorption occurs in larger pores, with reduced anisotropy in the adsorption potential.

The INS spectra for intermediate loadings (52 mbar and 100 mbar) are shown in Figures S7 and S8 of Supplementary Information. As expected, the results for intermediate loadings are in between those obtained for the lowest and highest loadings. At 52 mbar (3.65 mmol/g; $\theta_p = 0.11$) the quasielastic signal shows appreciable broadening at 77 K, and the splitting of the rotor peak is less prominent than at the lowest loading. Similarly, the high temperature broadening of the quasielastic signal is also observed at 100 mbar (5.14 mmol/g; $\theta_p = 0.16$), and the rotor peak looks similar to that at 167 mbar (6.73 mmol/g; $\theta_p = 0.21$).

Figure 5. Integrated intensity of elastic/quasielastic signal (a) and rotor peak (b) as a function of temperature and loading. Data at each temperature were normalized to the respective integrated intensity at 5 K (c, d). Error bars are less than the size of the symbols used. The lines are a guide to the eye.

The integrated intensity of elastic/quasielastic signal and the rotor peak at each loading is shown in Figure 5 as a function of temperature. The intensity of the elastic/quasielastic signal remains approximately constant below the supercritical temperature of bulk H₂ (33.14 K) at all loadings. This indicates that the population of immobile and partially mobile H₂ remains approximately constant up to about 33 K. However, the elastic/quasielastic intensity increases at higher temperatures. Moreover, if the constant loading data from Figure 5a are normalized to the respective integrated intensities at 5 K they all collapse on the same overlapping trend (Fig. 5c). This indicates that the proportional effect of temperature is caused by thermally induced para-ortho conversion.

It is worth mentioning that a prior QENS investigation of H₂ adsorbed on UMC showed that adsorbed H₂ species become mobile between 19 and 22 K [32] when the effective molecular size ($\rho = \sigma_o + \lambda_B$) of quantized light H₂ molecules dropped to values comparable with the wall-to-wall width of prevalent micropores in UMC (about 6 Å) [31]. Two factors determine the drop of ρ on the increase of temperature in conditions when the quantum effects cannot be neglected: The thermal wave length (de Broglie) of light H₂ molecules, $\lambda_B = h/(2\pi mk_B T)^{1/2}$, drops between 5.5 Å at 10 K to only 1.4 Å at 77 K. This variation also affects the C – H₂ interaction potential for quantized H₂ molecules and their equilibrium separation distance σ_o to the carbon surface. As a consequence, H₂ is “bulkier” than D₂ at cryogenic temperature, and moves slower on the increase of temperature, as proven by the delayed broadening of the quasielastic signal observed in QENS experiments [31]. Unfortunately that conclusion could not be strengthened by the results of the current experiment because the limited resolution of VISION spectrometer did not allow accurate analysis of the quasielastic signal broadening at such low temperatures.

The rotor peak area in Figure 5b shows an interesting variation with the temperature: At all surface loadings investigated all normalized curves are overlapped (Fig. 5d). Up to 25 K the integrated peak intensity decreases by about 20 % of its initial value at 5 K. At higher temperatures the drop in rotor peak area is faster, about 60 % of its initial value between 35 and 77 K. The drop in intensity of the rotor peak on increase of temperature is most probably caused by thermal induced mobility (rather than thermal desorption) since its temperature variation is essentially independent on the equilibrium pressure. At the two lowest pressures of these experiments bulk H₂ changes from solid directly to gas phase at about 13.7 K (Figure 1). At the two other pressures bulk H₂ passes shortly through a liquid phase on increase of temperature. The results in Figure 5 suggest that H₂ hosted in UMC ultramicropores at low loadings ($0.05 < \theta_p < 0.2$) has a different behavior. A rough analysis of pressure and temperature correlations at constant levels of rotor peak area (constant loading) using the Clausius-Clapeyron equation

$$\ln\left(\frac{P_1}{P_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (3)$$

indicates that the process is endothermic ($\Delta H > 0$). This is expected for a solid-to-liquid phase change. The enthalpy change at high loading (22.5 mmol/g; $\theta_p = 0.7$) is $\Delta H = 0.134$ kJ/mol, close to the latent heat of fusion of bulk hydrogen (0.116 kJ/mol), but smaller than the endothermic heat of para $\rightarrow$ ortho conversion (1.062 kJ/mol at 20 K). The enthalpy change was therefore identified with the latent heat of fusion for solid-like hydrogen hosted in carbon pores. At high loading a large fraction of adsorbed hydrogen resides in larger pores, and resembles solid H₂ at low temperatures. However, the enthalpy change increases as shown in Figure 6a at lower loadings, and reaches about 2.6 kJ/mol at 3.7 mmol/g ($\theta_p = 0.1$). At these low loading all hydrogen is trapped in ultramicropores and subject to a strongly anisotropic potential, as discussed above.

Figure 6b compares the rotor peak area measured at 77 K in all three series of experiments with the adsorption isotherm measured gravimetrically at the same temperature. The almost one-to-one agreement between the two was used to calibrate the arbitrary units used for integrated rotor peak area against the hydrogen loadings at 77 K. Figure 6a indicates that at all pressures investigated, a certain fraction (constant) of the amount adsorbed is held in narrow pores and is thermally converted to o-H₂. Unfortunately the calibration of rotor peak areas cannot be used for quantitative evaluation of elastic and quasielastic components obtained by deconvolution of the scattering signal close to zero energy. One reason is the large cross section difference between o-H₂ species, which are responsible for the elastic and quasielastic components, and p-H₂ species, which are quantified by the rotor peak area. Another reason is the unknown spectrometer response to events separated by almost 15 meV on the energy scale.

Figure 6: (a) Variation of fusion enthalpy of immobile H₂ adsorbed on UMC as a function of surface loading; (b) Comparison of rotor peak area of immobile H₂ at 77 K and the gravimetric amounts of adsorbed H₂ at the same temperature.

4.3 High Pressure Effect at 77 K

Figure 7 shows the results of the second series of experiments, where the behavior of adsorbed H_2 was examined from spectra recorded at 77 K and pressures between 0.1 and 40 bar. The background subtracted high pressure INS spectra are shown in Figure S9 of Supplementary Information. The quasielastic signal shows a visible increase with pressure. The strength of rotational peak also increases with pressure. For a quantitative analysis, the peak intensities were integrated between -2 meV and 2 meV (quasielastic) and between 10 meV and 25 meV (rotational peak). The baseline was subtracted from both the quasielastic signal and the rotor peak as shown in Figures S4 and S5 of the Supplementary Information.

Figure 7 Evolution of elastic/quasielastic signal (a) and rotor peak (b) as a function of pressure (0.10, 0.23, 0.51, 1.03, 3.25, 11.2, 22.4 and 40.0 bar) at 77 K.

In order to distinguish between the contributions from the solid- and liquid-like hydrogen, the elastic and quasielastic scattering signals need to be separated. This can be done using the

standard approach to analysis of quasielastic spectra, which is not normally performed at inelastic neutron spectrometers, but can be employed at VISION due to its sufficiently high energy resolution and intensity. The analysis involves fitting the data with a numerical convolution of the spectrometer resolution function, $R(w)$, with the model scattering function describing the diffusivity, $S(w)$, plus typically a linear fitted background. For the current system, the UMC sample measured prior to H_2 dosing was used for the $R(w)$ because it had no associated quasielastic scattering. A Lorentzian function describing a diffusion process was used for the $S(w)$. The resulting model fitted to the experimental intensity was thus

$$I(w) = C_0 \left[x \delta(w) + (1-x) \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + w^2} \right] \otimes R(w) + (C_1 w + C_2) = C_0 \left[x R(w) + (1-x) \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + w^2} \otimes R(w) \right] + (C_1 w + C_2) \quad (4)$$

Here the parameter x is the fraction of the elastic (vs. elastic plus quasielastic) scattering signal, which is associated with the solid-like immobile hydrogen. In turn, the fraction of quasielastic (vs. elastic plus quasielastic) scattering signal, $(1-x)$, is associated with the liquid-like partially mobile hydrogen. It should be noted that subtraction of the background spectrum, the UMC sample measured prior to H_2 dosing, from the fitted data is essential for accurate determination of the solid- and liquid-like H_2 contributions.

Figure 8. Comparison between H₂ excess adsorption, deconvoluted elastic and quasielastic signals, and total INS signal as a function of pressure at 77 K. Inset: Pressure effect on relative contributions of elastic and quasielastic signals.

Figure 8 shows the pressure dependence of integrated intensities obtained from deconvolution of elastic/quasielastic signals. Recall that the elastic and quasielastic signals originate, respectively, from the immobile (solid-like) and semi-mobile (liquid-like) hydrogen. Both signals increase sharply at pressures below about 1 bar, which is the range of initial micropore filling at 77 K. Using the Unilan isotherm fit, one can estimate that equilibrium hydrogen adsorption at 1 bar at 77 K results in about 50 % filling of total adsorption capacity. At these pressures adsorbed hydrogen exists both in solid- and liquid-like phase at 77 K, as shown by the elastic and quasielastic signals. At pressures above 1 bar

the elastic component remains (almost) constant and the growth of the quasielastic component bends slowly towards a saturation plateau at high pressures. Significantly, the sum of elastic and quasielastic signals follows consistently the adsorption isotherm measured gravimetrically (up to 20 bar) and the Unilan prediction (above 20 bar). The inset in Figure 8 shows the relative contributions of elastic and quasielastic signals. At very low pressure (100 mbar, $\theta_p = 0.2$) the two components have almost equal contribution, but as the loading increases the balance shifts rapidly and the liquid-like H₂ species dominate (75-80 %); The solid-like species still contribute about 20-25 % of total adsorption up to the highest pressures. Obviously, H₂ adsorbed at low loading is trapped first in ultramicropores (< 0.7 nm) where it remains immobile up to high temperatures. At higher loading adsorption continues in supermicropores (0.7 to 2 nm) and then in lower mesopores (> 2 nm), where a stable liquid-like phase was identified even at 77 K (Figure 8). The 20 : 80 ratio between elastic and quasielastic components reflects a similar ratio between the ultramicropores and the combined volumes of supermicropores and lower mesopores (see Figure S1 in Supplementary Information).

The secondary axis in Figure 8 shows the variation of the total signal intensity of the INS spectra integrated in the range of -2 meV to 1000 meV. The total intensity is proportional to total H₂ population in the sample cell and includes free H₂ gas along with adsorbed molecules, both partially mobile and immobile. Although the arbitrary units used for quantification of total intensity, elastic/quasielastic, rotor components are difficult to relate to each other, raw data (Figure 2) and area-integrated signals (Figure 8) show that the total signal intensity is much larger than the sum of elastic/quasielastic and rotor components. After an initial fast increase for pressures < 1 bar, the total integrated signal varies linearly at higher pressures. The fast initial increase at low pressure is mainly contributed by adsorbed solid- and liquid-like H₂ hosted in carbon. The linear increase at higher pressures reflects the

addition of more H₂ gas to the sample cell (free volume and UMC interparticle voids). The linear trend is expected from the equation of states of the free bulk gas.

4.4 Temperature Effect at Constant Pressure

The high temperature behavior of adsorbed H₂ was further monitored in the third experiment. The INS spectra were recorded at constant pressure (3.25 bar) and variable temperature (77, 110 and 150 K. The elastic/quasielastic signal at 150 K (Figure 9a) presents Fano-type resonance asymmetry. This is just due to slight over subtraction of the background signal; it is common in neutron scattering when two peaks slightly misalign and their relative intensities change. This particular case happens with the sample at 150 K (almost 5 times the critical temperature of molecular hydrogen) and the background measured at 77 K. The background does not affect the shape of the peak at 110 K, but it slightly over subtracts at 150 K. The integrated intensity of the difference spectrum signal at 150 K is very small, so one cannot claim that there is appreciable elastic/quasielastic signal at this temperature. No immobile or partially mobile H₂ exists at this temperature.

Figure 9. Elastic/quasielastic signal (a) and rotor peak (b) at 3.25 bar at high temperatures. Well-defined elastic/quasielastic and rotor peak exists up to 110 K.

However, the elastic/quasielastic signal from immobile and partially mobile adsorbed H₂ is clearly observed at 77 and 110 K, well above the pressure-corrected boiling temperature of free gas (25 K) at 3.25 bar. Moreover, the rotor peak (solid-like, immobile H₂) is visible at 77 K and even at 110 K. This fact indicates that liquid- and solid-like hydrogen subsists in UMC pore systems at temperatures much higher than the critical point of bulk H₂ (33.14 K). The two peaks vanish at 150 K indicating that hydrogen was desorbed.

4.5 The density of adsorbed hydrogen

Figure S1 of Supplementary Information shows porosity distribution in UMC material, both in terms of pore volume and in terms of internal pore surface variation with the wall-to-wall pore width in slit shaped pores. This is the effective pore width available to hosted molecules. The porosity distribution was then correlated with the Unilan fitting of excess adsorption isotherms (Figure S2) at 77 K in an attempt to estimate the relationship between the amount adsorbed (mmol/g) at every equilibrium pressure and the corresponding pore size (or volume) available for hosting the adsorbed phase. Using eq. (S2) from Supplementary Information, the surface area occupied by the adsorbate (S_P) was estimated at each equilibrium pressure. Then the porosity distributions for internal pore surfaces, $S = S(d)$, and pore volumes, $V = V(d)$, shown in Fig. S1 were correlated to determine the maximum pore width d_P and the corresponding pore volume, V_P , that contains the adsorbed phase at every equilibrium pressure P . The implicit assumption of this procedure is that, on a patched surface consisting of a multitude of energetically uniform domains, different groups of sites are occupied in the

decreasing order of their adsorption potential, which follows the *increasing* order of corresponding pore widths. Lastly, the equilibrium amounts adsorbed at every pressure, q_P , were correlated with the corresponding pore volumes used at that pressure, V_P , to estimate the effective density of the adsorbed phase hosted in pores of size d_P .

Figure 10: Effective hydrogen density in pores of various sizes at 77 K as a function of equilibrium pressure and pore width. The source for solid and liquid bulk H₂ density is [37].

The results (Figure 10) show that the effective density of adsorbed hydrogen decreases with the increase of pore width and with the increase of pressure. For comparison, the density of bulk solid H₂ and liquid H₂ at triple point and critical point are marked by horizontal lines in Figure 10. These plots support the conclusion of this neutron scattering study: At 77 K and

pressures below 1 bar the effective density of hydrogen in ultramicropores is comparable to that of solid H_2 . In this range of low loadings (experiments from series 1 and low pressure data from series 2) the adsorbed phase experience high densification in ultramicropores, as theoretically predicted [63,64] and inferred from experiments [65] by others. The pressure range where solid-like density predicted by this estimation drops rapidly coincides with the initial pressure range where sharp drop was seen in the elastic contribution to total neutrons scattering (inset in Fig. 8).

Data at 77 K from the second (and third) series of experiments show a different behavior. Starting from pressures above 5 bar the estimated effective density of adsorbed hydrogen matches the density of liquid H_2 and drops slowly at the increase of external pressure. At these pressures H_2 is hosted in gradually larger pores that, along with ultramicropores, also include supermicropores and (at the highest pressures) the narrow mesopores. Fig. 8 shows that the surplus of adsorbed H_2 condenses in liquid-like phase, which is now dominant, but a solid-like phase subsists at 77 K up to the highest pressure. The effective density is therefore an average value over pores of various sizes.

5. Conclusion

The main finding of this investigation is the persistence of solid-like (immobile) and liquid-like (partially mobile) H_2 confined in carbon pores at temperatures and pressures remote from the critical point of free H_2 gas. The presence of high-density, mobility-restricted phases (liquid-like and solid-like) at supercritical conditions is a general behavior of H_2 confined in carbon nanopores. Solid-like and liquid-like H_2 subsist up to 40 bar at 77 K and their ratio reflects the pore structure of the adsorbent. They diminish by desorption at higher

temperatures, as expected, but solid-like H₂ is present even at 110 K and 3.25 bar pressure, in conditions where bulk hydrogen exists only in gas form.

At the start of this study, the expected main output of VISION spectrometer, a state-of-the-art instrument optimized for vibrational spectroscopy, was the qualitative exploration of phase behavior of confined H₂ as function of loading, temperature and pressure. However, later it became clear that more information could be extracted from this spectrometer. Thus, analysis of rotor peaks showed that the strongly anisotropic adsorption potential at the strongest adsorption sites (low coverage) becomes gradually more isotropic at higher coverages (weaker sites). Analysis of the broadened signal near zero energy transfer and deconvolution of the quasielastic component from the elastic component could also be performed, albeit within some instrument limitations. This analysis by itself pushes the limits of what was previously thought to be possible in vibrational indirect geometry spectrometers optimized for inelastic energy transfers commensurate with molecular vibrations. The relative proportion of mobile and immobile H₂ species as a function of surface loadings, estimated from this analysis, revealed strong correlations with the pore structure of the carbon support. However, the line broadening of the quasielastic component as a function of temperature, and its Q dependence, could not be analyzed during these experiments. Such analysis would have been indeed relevant for determination in minute details of the diffusion mechanism.

In conclusion, the significance of present results reaches beyond the immediate interest in adsorption theory and confined fluids behavior. They may infuse in new impetus onto the search for the optimal hydrogen storage material, and underline the need of further efforts for developing ultramicroporous carbon materials with large volumes of narrowly distributed pores sizes, preferably close to the sub-nanometer size of hydrogen molecules.

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