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Molecular hydrogen in porous Vycor glass

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Raman measurements were performed of the lowest rotational $J=0\rightarrow 2$ and the intramolecular vibrational transition of p-H_2 confined in a Vycor rod. From the dependence on the amount of H_2 adsorbed in the system, we are able to assign specific features in both spectra to molecules which are in contact with the surface. Studies of the temperature dependence show that below 12 K, the system is in a metastable state, which may result in a suddenly freezing in of the molecules, evidenced by a quenching of both transitions. For sufficiently slowly cooled systems, the molecules are able to orient into a phase which is neither hcp nor fcc. Evidence for the occurrence of islands of H_2 is provided. For the smaller filling fractions, our results show that a part of the adsorbed molecules may remain in the liquid phase down to lower temperatures than so far observed.

I. INTRODUCTION

The properties of liquids confined in a porous medium are substantially modified. Phase transitions in particular can be strongly affected by the interaction with the pore surfaces. Despite the random nature of the porous media used, sharp, well-defined critical behavior is often observed.[1] In this paper, the effect of confinement in porous Vycor glass[2,3] will be studied. Vycor was chosen as it is a material which is very well characterized[3,4] and its pore size distribution, centered around 60 Å diameters, is rather monodisperse. This property was proven to ease substantially the interpretation of the experimental results.[5] As the dimensions of the pores in porous Vycor are small compared to the wavelength of visible light, Rayleigh scattering is minimized. Optical spectroscopy is therefore a well suited method to study the effect of confinement.

Bulk liquid p-H_2 condenses at 13.8 K. When confined in porous Vycor glass, the freezing temperature is strongly reduced to 9.3–9.5 K, as shown by heat-capacity measurements.[6,7] Recently, these elaborate studies were extended to partial filling fractions,[8] thermally treated Vycor (to reduce the average pore size),[8] and extremely slow cooling rates.[9] In the small pore and the Vycor filled for less than 63%, no freezing transition could be resolved. Additional features appeared for the slowest cooling procedure.

In contrast to the large number of macroscopic measurements on this system,[6–9] almost no microscopic characterization of this system has been performed so far. Infrared-absorption measurements of the vibrational transition and higher energy overtone transitions of the H_2 molecule proved possible by surface enhancement effects. Their experimental resolution, however, was not sufficient to resolve the features we will be discussing and measurements were performed using n-H_2. Neutron diffraction of n-D_2 in Vycor showed clearly the presence of amorphous components.[10] The intermolecular interaction between H_2 molecules is less compared to D_2, resulting in a larger effect of disorder and confinement on the crystalline phases for H_2. One of the problems we will be discussing in this paper is the role played by the pore-solid interface in the solidification process.

In this paper, we will present results of Raman measurements of the lowest rotational, $J=0\rightarrow 2$ (354 cm^{-1} for liquid bulk p-H_2, Ref. 11), and intramolecular vibrational transition, $\nu=0\rightarrow 1$ (4153.8 cm^{-1} for liquid bulk p-H_2, Ref. 12), of p-H_2 confined in a Vycor rod. These transitions have been well studied in the bulk liquid[12] and solid[13,14] phase and have a large cross section for Raman scattering. The interaction with the surface does not mix the nuclear spin states which are used to identify the ortho and para species. The large cross section allows us to study very small filling fractions, down to 0.8% H_2 molecules, which are physisorbed on the large surface area (about 250 m^2/g) of the Vycor. From the surface density of a monolayer $n=0.12$ Å^{-2} (Ref. 15), one determines the needed H_2 fraction to be 22%. Hence, filling fraction of one fortieth of a single monolayer coverage can be studied with this technique. Nucleation centers for solidification of the hydrogen which may be present in the sample compartment include bulk solid surrounding the Vycor rod and larger pores having a diameter of 120 Å, for which recently evidence was provided by accurate adsorption isotherm measurements.[8] To eliminate the presence of both, filling fractions up to only 95% were investigated (although the term "completely filled" will be sometimes used).

Our measurements show that Raman spectroscopy, although rarely used in this field, is a very powerful technique for the study of physisorbed molecules and the effects of confinement. In particular, we will show that this technique allows one to (i) assign the different peaks in the spectrum to different layers of H_2 on the Vycor material; (ii) provide evidence for the formation of islands of adsorbed molecules on the surface; (iii) estimate the adsorption potentials; (iv) probe the structural phase of the confined molecules; (v) evaluate hysteresis effects.

The paper is organized as follows: Sec. II provides details on the experimental environment, needed for a good temperature stability and the treatment of the Vycor and the p-H_2. In Sec. III the experimental results for the different filling fractions and cooling procedures will be presented. A

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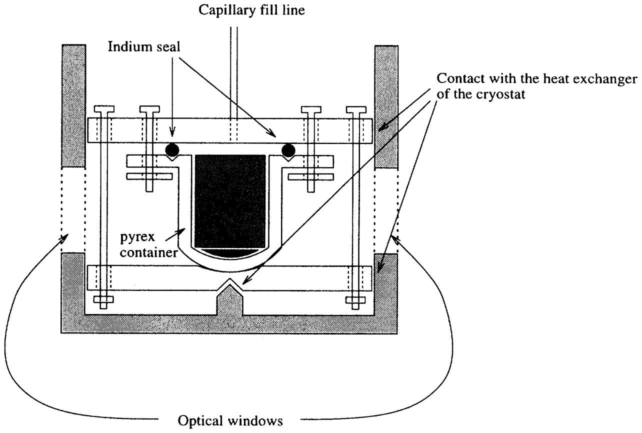

FIG. 1. Cross section of the mounting of the Vycor material in the interior part of a helium flow cryostat suitable for optical spectroscopy. The whole setup has, apart from the three optical windows and the fixing screws, a cylindrical symmetry around the fill line.

discussion and interpretation of the observed phenomena follows in Sec. IV. Section V summarizes the obtained results.

II. EXPERIMENTAL

The Vycor material was boiled repeatedly in 30% solutions of hydrogen peroxide for several hours, then rinsed in deionized distilled water and carefully evacuated.[16,17] No thermal treatment to reduce the pore sizes was performed. The sample rod (1.327 g) was inserted in a pyrex container (see Fig. 1), which was tightly fitting the Vycor in order to eliminate possible contributions from bulk H_2. A small amount of indium reduced the void due to the curvature of the bottom of the pyrex cell. Extreme care was taken to ensure a uniform temperature throughout the sample by clamping the container between two pieces of brass, which were in close contact with the heat exchanger of a helium flow cryostat. Temperature uniformity was further enhanced by interconnecting these two brass pieces by bars and adding a small amount of helium contact gas. No temperature variations were seen in subsequently recorded spectra, indicating that no temperature gradients were present in the system. As this was observed in the fast cooled sample, this *a fortiori* true for the slowly cooled sample.

Research grade H_2 gas (99.9999% pure) was converted to para-H_2, using Apachi gel as a catalyst[13] and was allowed to flow into the Vycor by a capillary fill line. By monitoring the pressure in a calibrated volume, the amount of H_2 added to the Vycor was varied. As some H_2 molecules are adsorbed firmly to the surface, the Vycor material was heated up to room temperature in between experimental runs to ensure a complete desorption of the H_2. This procedure was proven to be efficient, as was verified by Raman scattering. The concentration of o-H_2 in the Vycor was determined by spontaneous Raman scattering[13] off the lowest $\Delta J=2$ rotational transition of both ortho and para species and was found to be less than 1%.

Light from an Ar laser (514.5 nm) was focused in the center of the sample. As only scattered light of the focus is collected in a 90° orientation, no contribution of the bulk H_2 can be expected. The scattered light was analyzed using a triple monochromator and detected by a CCD array. Experimental resolution varied between 0.35 and 2.0 cm^{-1}. Absolute frequency positions are determined with an accuracy of 0.5 cm^{-1}.

Raman scattering off the empty Vycor is in agreement with previous measurements at higher temperature.[17,18] Sublimation of the H_2 molecules proved to be a serious problem when heating the system up from lower temperature. Therefore, no measurements could be performed at elevated temperatures as the pressure in the capillary fill line increased very fast above 13.5 K.

III. EXPERIMENTAL RESULTS

A. Different filling fractions

Raman measurements were performed for very small amounts of H_2 molecules adsorbed onto the surface. Therefore, the molecules were brought into contact with the Vycor at an elevated temperature of 32 K, where the H_2 molecules are well within the gas phase. Measurements were performed at 13.2 K. No temperature dependence of the rotational and the vibrational transition was observed for small filling fractions. After each set of measurements, the system was heated up slowly to 32 K and an additional amount of H_2 gas was added. The Vycor rod was left *in situ*, allowing for an easy comparison between the results for the different filling fractions which were investigated: 0.8, 1.5, 3.1, 5.4, 7.6, 10, 13, 19, and 25%.

Figures 2 and 3 show the experimental results obtained for the $J=0\rightarrow 2$ rotational and the $\nu=0\rightarrow 1$ vibrational transition, respectively. For the smallest filling fraction of 0.8%, lines at 309.6, 325.8, 333.1, and 383.9 cm^{-1} in the rotational region can be distinguished, each having a different line shape. For higher filling fractions, a broad band develops in the rotational region, reaching from 305 up to 415 cm^{-1}. This band can already be clearly distinguished for 5.4% of H_2. The overall intensity of this broad band increases up to a filling fraction of 19% H_2. The peaks at 325.8 and 333.1 cm^{-1} grow strongly in intensity, while the peak at 309.6 cm^{-1} develops into a broad shoulder towards lower frequencies of the former two bands. Not yet present in the spectrum for 13% H_2 content, an intense peak develops at 354 cm^{-1} for 19% H_2 present and becomes stronger with still increasing H_2 content, as is clear for 25% (Fig. 2) and for the completely filled Vycor (see Sec. III B).

The vibrational transition (see Fig. 3) shows for the smallest filling fraction of 0.8%, a broad transition at 4130 cm^{-1} and a narrower peak at 4138 cm^{-1}. The first peak grows up to 5.4% H_2 content and remains constant for higher filling fractions. As the high-frequency peak continues to grow in intensity, the first peak becomes a shoulder of it. The frequency of the most intense peak shifts to larger values for increasing filling (4138.8 cm^{-1} for 5.4%, up to 4144.6 cm^{-1} for 25%). Note that almost all vibrational frequencies are below 4153.8 cm^{-1}, the bulk liquid value, while the distribution of rotational transitions is more or less symmetrical around the bulk value of 354 cm^{-1}. At the frequency of the bulk liquid transition, a weak shoulder can be

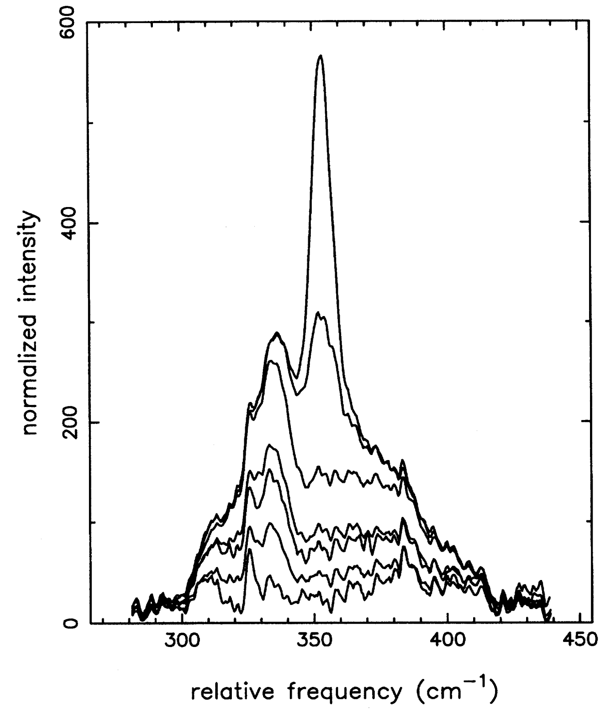

FIG. 2. Raman spectrum of the $J=0\rightarrow2$ rotational transition for minor filling fractions of the Vycor rod with H_2 molecules. Measurements were performed at 13.2 K with an experimental resolution of 2.3 cm^{-1}. Representative data shown correspond to filling fractions of 0.8, 5.4, 10, 13, 19, and 25% of the entirely filled Vycor from the bottom to top graph. Part of the noise on the data is due to (minor) variations in sensitivity of the CCD device.

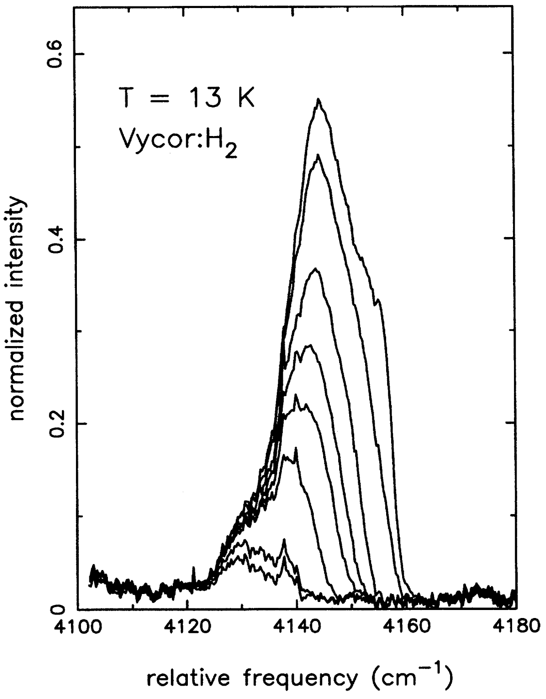

FIG. 3. Raman spectrum of the $\nu=0\rightarrow1$ vibrational transition for small filling fractions of the Vycor rod with H_2 molecules. Measurements were performed at 13.2 K with an experimental resolution of 1.4 cm^{-1}. Representative data shown correspond to filling fractions of 0.8, 3.1, 5.4, 7.6, 10, 13, 19, and 25% of the completely filled Vycor from the bottom to top graph.

observed for 25% of H_2. Increasing the H_2 content up to 33% (see Fig. 4), a narrow peak appears and becomes very intense for the completely filled Vycor (see Sec. III B).

We have explicitly verified the temperature dependence of both transitions for filling fractions of 17 and 33% and for the completely filled system. No temperature dependence between 4 and 14 K was found of the scattered light, except for the peaks appearing at the frequencies of the corresponding transitions in the bulk liquid H_2. Before we digress on this behavior, we will discuss the effect of the applied cooling procedure on the obtained spectra.

B. The effect of the cooling rate

The two cooling rates studied are well described by an almost linear dependence of the temperature on the elapsed time and correspond to a temperature decrease from 16 to 7 K over 3 and 11 h, respectively. The vibrational transition in the slowly cooled sample [see Fig. 5(b)] shows at 9.5 K a narrow intense line at 4153.6 cm^{-1} and a broad, less intense transition at lower frequency with a maximum at 4144.6 cm^{-1}, in agreement with Sec. III A. When slowly cooling down [Fig. 5(b)], no noticeable change in the Raman spectrum could be resolved down to 9.5 K. At 9 K, the intensity of the narrow peak at 4153.6 cm^{-1} decreases and another sharp peak starts appearing at 4152.4 cm^{-1}. At 7.5 K, only the latter line remains. Further cooling does not reveal a change in the recorded spectrum. When warming the system up, we observe a return to the original situation at high temperature, as seen in Fig. 5(a). The shift of the narrow vibrational transition occurs (i) over a much broader temperature interval and (ii) towards higher temperatures, i.e., 10–13.2 K. In marked contrast with this, the vibrational transition in the faster cooled sample (see Fig. 6) does not show any jump in vibrational frequency. Instead, the intensity of the narrow peak decreases strongly with decreasing temperature and an asymmetry towards higher frequencies develops. When increasing the temperature, the narrow peak "regains" its intensity.

Figure 7 shows the added integrated intensity of both narrow peaks for the slowly cooled sample as a function of the temperature. To eliminate the contribution from the broad transition to this quantity, a constant was subtracted corresponding to the integrated intensity of a scaled spectrum which was obtained for a small filling fraction showing no narrow feature. It is clear that this quantity remains almost completely constant during the whole cycle of cooling and warming. The decrease in intensity above 12.5 K during the heating process is due to local sublimation of H_2 molecules. In Fig. 8 we drew the corresponding quantity for the fast cooled system, 67% filled, Vycor. A clear hysteresis behavior is seen. The temperature region over which this occurs, was seen to depend on the particular run.

For the rotational transition, we observe the following behavior. At 14 K, the spectrum [see Figs. 9(a) and 9(b)] consists of a narrow (354 cm^{-1}) and a broad transition underlying the latter (in agreement with Sec. III A). When slowly cooling the material down, the narrow peak shifts slightly to higher frequencies and splits into two components, with a splitting of $\sim 1.6\ cm^{-1}$ [see Fig. 9(a)]. This occurs at the same temperature as the shift in the vibrational frequency. Using the faster cooling procedure [Fig. 9(b)], a strong reduction of the intensity of the narrow peak is observed, which starts at about 8 K. When warming the sample up, the integrated intensity of the narrow peak shows a hysteresis effect as a function of the temperature, which for the 67% filled system was verified to have the same shape as Fig. 8.

C. Extra vibrational feature

Our high-resolution measurements show the presence of an additional vibrational transition, which was only observed for the completely filled Vycor. In the slowly cooled sample (same experimental run as for Sec. III B), as shown in Fig. 10, an extra peak can be clearly seen at 4150.6 cm^{-1} which decreases in intensity with decreasing temperature and vanishes at a much higher temperature than the effects discussed in Sec. III B. We observe no recovery of the intensity with increasing temperature. In the completely filled and fast cooled sample, it is only present as a wing to the sharp transition, as these measurements were performed with a lower resolution. This makes a further analysis of the latter results as a function of temperature hardly impossible. This transition is not present for the partial filling fractions.

D. Cooling of partial filling fractions

The intensity of the narrow vibrational transition for the 17% filled Vycor is too small for an analysis as a function of temperature. Besides this, no difference in temperature dependence of the narrow rotational and vibrational transitions can be seen. In Figs. 8, 11, and 12, the integrated intensity of the narrow rotational transition for 67, 33, and 17% filled Vycor respectively, is plotted as a function of temperature and for both cooling and heating of the sample. These partial filling spectra were obtained applying the faster cooling procedure. Upon cooling, the integrated intensity decreases and becomes at a specific temperature equal to the value obtained when warming up. If we define that temperature as the freezing temperature for the complete system, we see that this temperature decreases as a function of the filling fraction. The size of the hysteresis effect decreases in a similar way.

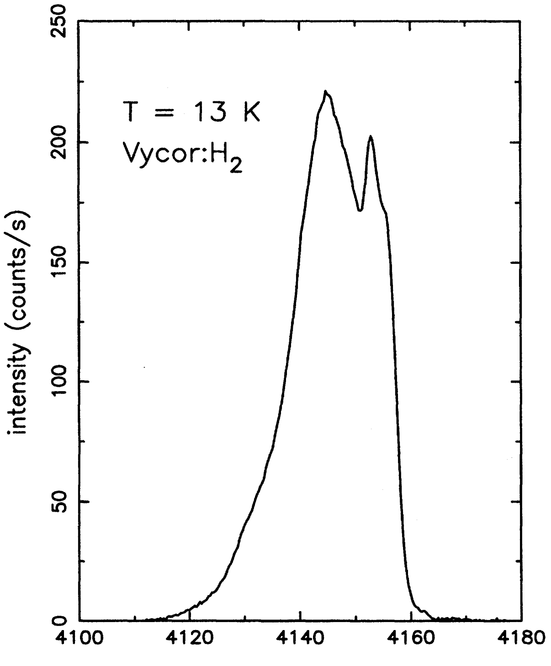

FIG. 4. Raman spectrum of the vibrational transition of 33% filled Vycor glass. Experimental resolution yields 1.4 cm^{-1}.

IV. DISCUSSION

A. Adsorbed layer

The $J=0\rightarrow 2$ rotational transition of adsorbed p-H_2 molecules is greatly distorted from that of a molecule in the liquid or the solid phase. However, only a rotational transition around $6B$ (B being the rotational constant) is observed

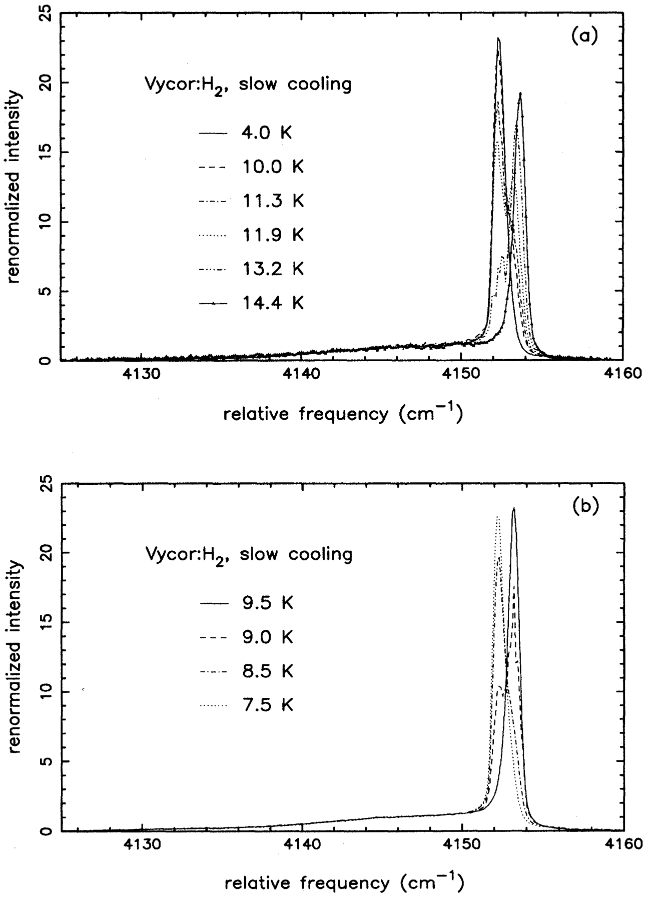

FIG. 5. Raman spectrum of the vibrational transition of Vycor filled with para-H_2 for the slowly cooled sample. (a) and (b) were obtained while warming up and cooling down the sample, respectively. In the temperature intervals 16–9.5 K and 7.5–4 K for (b) and 4–9 K and 14.4–16 K for (a), no change in line shape was observed. Spectral resolution is 0.35 cm^{-1}.

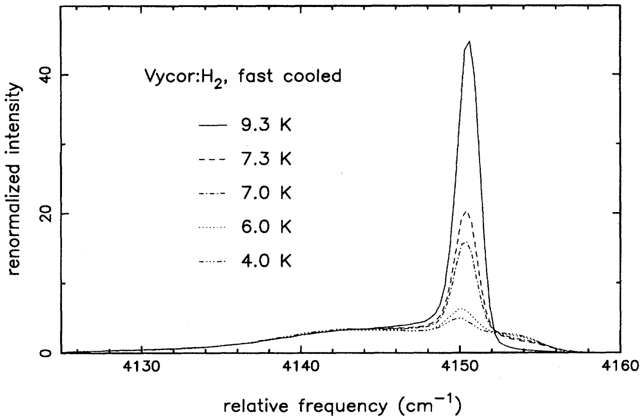

FIG. 6. Raman spectrum of the vibrational transition of Vycor filled with p-H_2 using the fast cooling procedure for different temperatures while cooling down the sample. Spectral resolution yields 1.7 cm^{-1}.

and no intensity could be detected around B and $4B$, as would be the case for extreme hindrance of the rotational motion.[19,20]

A rotational transition at the same transition frequency as for bulk liquid p-H_2, at 354 cm^{-1}, appears only for the larger filling fractions and for the completely filled pores. For H_2 fillings above 25%, the intensity of this peak grows while the broad band does not show any change in intensity. We can therefore assign the transition at 354 cm^{-1} to the p-H_2 molecules which are not in direct contact with the surface of the confining material. They do not experience a detectable shift of the rotational frequency. The broad band corresponds to H_2 molecules experiencing an interaction by the surface while being in the first or second adsorbed molecular layer. One can make a similar reasoning for the vibrational transition, assigning the broad band (at 4144.6 cm^{-1} for the completely filled Vycor) to the first and possibly second layer of adsorbed molecules and the narrow transition at the bulk liquid frequency to the unperturbed molecules in the center of the pores.

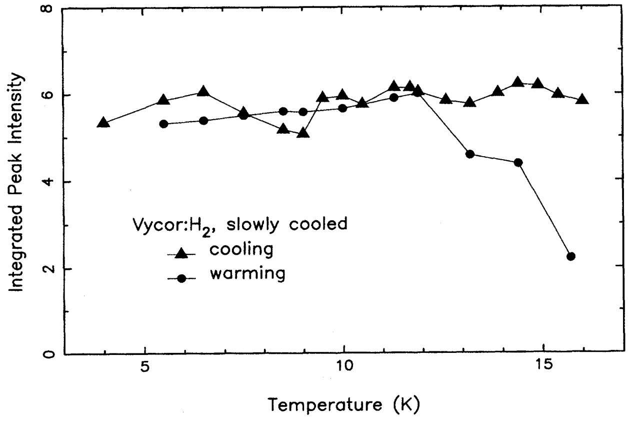

FIG. 7. Added integrated intensity of both narrow peaks in the vibrational spectrum for the completely filled Vycor when applying a slowly cooling procedure. Sublimation of H_2 molecules is responsible for the decrease in signal above 12.5 K during the heating process.

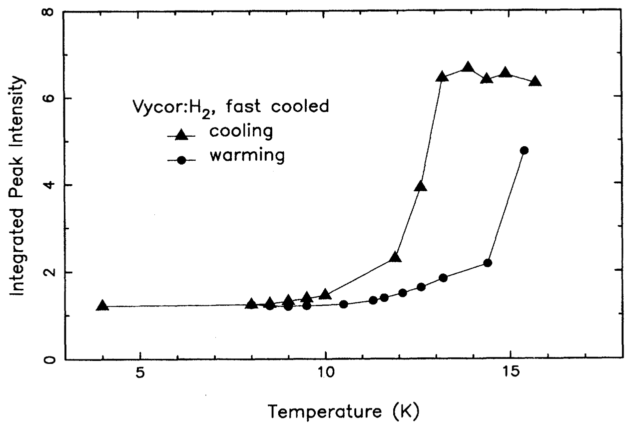

FIG. 8. The integrated intensity of the narrow peak in the vibrational transition for the 67% filled Vycor when applying the relatively fast cooling procedure. No measurements were performed at higher temperatures due to sublimation of the H_2 molecules.

The absence of any temperature dependence of both signals from the adsorbed molecules indicates no essential change in interaction over the whole temperature interval studied. The melting temperature, determined from specific-heat measurements, was seen not to apply apparently to the first layer of molecules. This explains why only a fraction of the H_2 was seen to contribute to the latent heat, resulting in a lower entropy associated with the melting than expected.[7]

B. Island formation

Figure 3 shows that with increasing H_2 content a gradual filling of the broad vibrational transition occurs from lower towards higher frequencies. As the pores in Vycor have a tortuous and complicated geometry, one may expect to find a continuous distribution of surface potentials. This continuous distribution of interaction sites can be related to essentially two origins: (i) the dispersion of the pore sizes is not vanishing, but small, as was observed experimentally;[4,8] (ii) the pore size distribution limits only in one dimension the curvature of the surface. It does not impose any restriction on the other dimension and one may expect a different surface potential in a torus than in a linear channel. This is especially important for Vycor, as its chord size distribution is much broader than the pore size distribution and is only slightly shifted towards higher values.[4]

Molecules will first adsorb to sites with the highest adsorption potential, corresponding to the largest shift in vibrational frequency (see Fig. 3). In our Raman spectra, we see that for increasing filling fractions, the vibrational frequencies of the adsorbed molecules shift closer towards the bulk value, indicating that the adsorption potentials are lower. For small filling fractions, islands are formed where the adsorption potential is strongest. Contributions of roughness on the atomic scale also play a prominent role by determining the size of these islands. The broad distribution of surface potentials may result in growth of a second layer before completion of the first layer.[8]

Infrared measurements[15] showed a shift of the vibrational frequency of 31 cm^{-1}, corresponding to an adsorption potential of 620 cm^{-1}. In our measurements, we observe a broad distribution of vibrational transitions rather than a narrow peak, which has a maximum shifted over only 9.2 cm^{-1}. The lower edge of the broad transition corresponds to 4125 cm^{-1}, indicating that the frequency shift and calculatedadsorption potential in Ref. 15 is substantially overestimated. This may be due to a stronger interaction with the surface of the n-H_2 gas they were using through the electrical quadrupole moment of the o-H_2 constituent. If we take the averaged value of 4144.6 cm^{-1} for the vibrational frequency of the adsorbed molecules, we can deduce the relative deviation[15] of the equilibrium intramolecular distance, $r_e = 0.74$ Å given by $(r_{es} - r_e)/r_e = 2 \times 10^{-3}$. This corresponds to a very small modification of the molecule. The resulting adsorption potentials are about half or one-third of their results, yielding values close to the typical adsorption potential of 300 cm^{-1} for H_2 of surfaces.

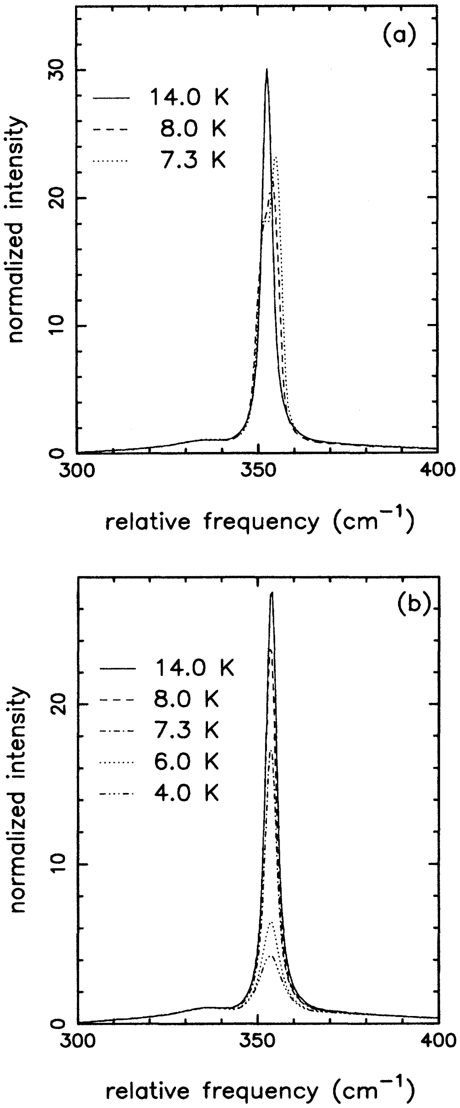

FIG. 9. Raman spectrum of the rotational transition of p-H_2 in the completely filled Vycor for a slowly cooled (a) and fast cooled (b) sample for different temperatures. Measurements were performed during the cooling procedure. Spectral resolution is 1.6 cm^{-1} and 2.0 cm^{-1} for (a) and (b), respectively. For (a), no change of the line shape was observed from 16 to 9.5 K and 7.5 and 4 K.

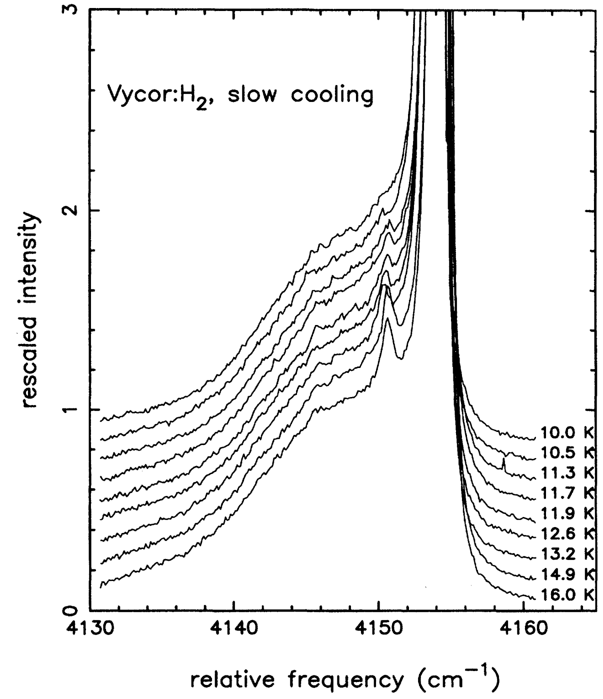

FIG. 10. Vibrational frequencies in the slowly cooled, completely filled, Vycor as a function of temperature. A transition at 4150.6 cm^{-1} has a different temperature dependence than the bulk contribution at 4153 cm^{-1}. Spectral resolution is 1.7 cm^{-1}. The data have been shifted vertically to allow for a good comparison.

In the rotational spectrum, a discrete number of well separated bands appears instead of a single rotational transition for the smallest amount of adsorbed molecules, i.e., 0.8% H_2. For higher filling fractions, the distribution of transition frequencies becomes continuous with some peaks at specific transition frequencies. Apparently, our results for the rota-

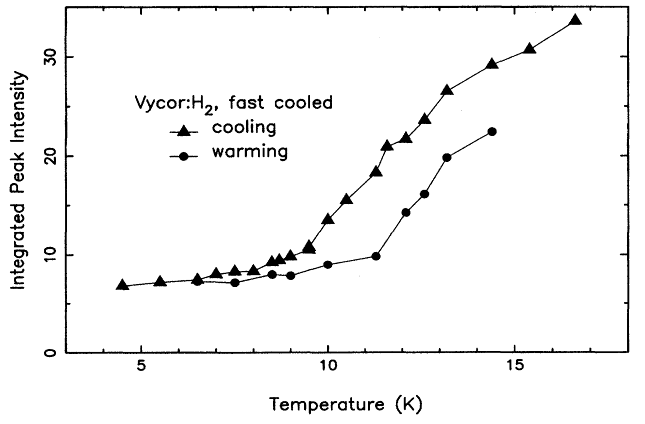

FIG. 11. Same as in Fig. 8, but for 33% filled Vycor and the rotational transition.

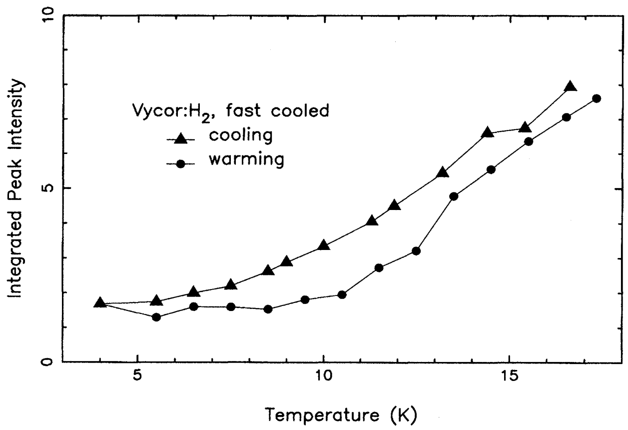

FIG. 12. Same as in Fig. 8, but for 17% filled Vycor and the rotational transition.

tional transition as a function of the filling fraction are in disagreement with the "island" formation idea,[8,21,22] which is clear from the vibrational transition. This reasoning assumes a similar effect of the surface potential on the two transitions, which are of a different character. Note in this respect that (i) the appearance of an unperturbed liquid signal in the vibrational spectrum starts at a higher filling fraction compared to the rotational transition and (ii) the different effect of the surface potential on both transitions is also evidenced in a different span in frequencies, i.e., about 110 cm^{-1} for the rotational transition and 40 cm^{-1} for the vibrational transition. To demonstrate this different behavior, a molecule with the intramolecular axis normal to the surface will experience a larger effect on the intramolecular vibration than on the rotational transitions.

The appearance of peaks in the rotational transition point to a larger frequency of occurrence for specific sites in the material. They are already present for low filling fractions, indicating that these sites have a sufficiently large adsorption potential. It is tempting to assign them to special sites in the tortuous geometry of the porous medium, as, e.g., the smallest pores or strong curvatures near junctions.

The wagging motion of surface Si-OH, at 380 cm^{-1} for the empty Vycor, may couple with the rotational transition of the H_2 molecules, having a nearby transition frequency. Whereas this surface mode is only infrared active for unadsorbed Vycor,[17] it may show up in the Raman spectrum by coupling to the $J=0\rightarrow 2$ transition of the adsorbed H_2 molecules. The scattering intensity at frequencies above the bulk liquid value is probably too high to be caused by such an effect, but we cannot *a priori* eliminate it.

C. Structural transition

Using the slow cooling procedure, we observe (see Fig. 5) a jump in the vibrational frequency of 1.2 cm^{-1} from the bulk liquid value which is of the same order of magnitude as the shift,[12] occurring at the transition from bulk liquid to bulk hcp solid, 1.92 cm^{-1}. The transition temperatures when cooling and warming correspond to the melting and freezing temperatures determined by heat-capacity measurements,[6,8] yielding a similar hysteresis effect.

For the rotational transition we observe at the same temperature a small shift in frequency towards larger values and a splitting of the peak into two components, separated by 3.7 ± 0.4 cm^{-1}. As both features are clear indications of a structural phase transition, it is not clear what the low-temperature phase of the confined H_2 is. The key in assigning a structure lies in the presence of a rotational doublet. If the transition would occur to an hcp solid, three peaks with a mutual separation of 2 cm^{-1} are expected.[23] A transition to an fcc structure would result in doublet split by 7 cm^{-1}, however (Ref. 11). Hence for sufficiently slow cooling rates the molecules are able to condense into a structurally ordered phase, which is neither the hcp, nor the fcc phase. These results are real evidence that depending on the cooling rate, a different microscopic behavior of the H_2 molecules is obtained.[9]

It was assumed that in the smallest pores of the Vycor material, the H_2 molecules may remain in the liquid state down to the lowest temperatures. From the absence of any detectable signal intensity at the wavelength of bulk liquid transition in the vibrational spectrum of the slowly cooled system, we can conclude that no liquid H_2 is present in the completely filled Vycor. This is only true provided that the interaction with the surface does not shift the liquid transition frequency.

For the relatively fast freezing rate, we observe no shift in vibrational or rotational frequency but a strong reduction of the signal intensity. In this case, the molecules are not able to order during the freezing in and an inhomogeneous broadening of the vibrational transition occurs. The sudden freezing did not occur at one reproducable temperature, but was seen to vary from one run to another. If we define the freezing temperature as corresponding to half the reduction in the integrated intensity, the range of freezing temperatures observed was (7.3–12) K. In Fig. 6, a rather high freezing temperature is shown for the 67% filled Vycor. No direct correlation of the freezing temperature with the filling fraction nor cooling rate could be determined. Hence, we believe the spread in freezing temperatures is related to the metastable character of the undercooled H_2 liquid, which can freeze in suddenly by a small perturbation of the system. The temperatures found by the heat-capacity measurements,[6,8] 9.3 and 8.5 K, are within the range specified by us. We found a corresponding melting temperature of ~ 14 K, higher than the 11.4 K of the heat-capacity measurements.[6]

The decrease of the intensity of the rotational transition with decreasing temperatures may be due to an increasing axially confining potential which in an extreme case can restrict the molecule from rotating.[19] At first sight it is remarkable, considering the large zero-point motion of the H_2 molecule in the solid phase, that macroscopic time scales are needed for the system to order into one particular structure. During the cooling process, the molecules have to overcome the barriers to domain growth which are caused by the interconnected and tortuous geometry of the pores. This is especially important for Vycor as the distance between junctions is comparable to the pore size.[4] For the related problem of domain growth in a binary liquid mixture contained inside a porous medium, one has found a substantial slowing down of the growth process when the average size of the domains became comparable to the average pore size.[24,25] Recently interpore correlations were seen to play an important role for D_2 in Vycor, where much larger crystallite sizes were detected than the nominal pore dimensions.[10,26]

D. Vibrational transition at 4150.6 cm^{-1}

Heat-capacity measurements showed also the presence of a second freezing temperature of H_2 in the Vycor pores at 12.4 K, which was related to freezing in larger pores with a radius of $\approx$ 60 Å.[8] This anomaly in the heat capacity was only found for completely filled pores, which we correlate with the presence of an extra vibrational transition at 4150.6 cm^{-1} in our experimental results (Sec. III C). If we define the transition temperature as the temperature at which no discernable intensity is present, we obtain 10.5 K, which is lower than the temperature found in the heat-capacity measurements. This disagreement in transition temperature may be related to differences in size of the larger pores in the system, although this is not likely to be so, as only minor changes in transition temperatures were observed for different Vycor samples.[8]

E. Monolayer fillings

No temperature dependence was found for the lower filling fractions, except for the transition of the molecules in the liquid phase, which are not in contact with the surface. The integrated intensities of the narrow peak for 33 and 17% (see Figs. 11 and 12, respectively) clearly show a similar behavior to that observed for the faster cooled 95% filled system. This observation is apparently in contrast with heat-capacity measurements which did not resolve any freezing transition for filling fractions lower than 63%.[8] This discrepancy is probably related to (i) a variation of the freezing transition due to the distribution of interaction potentials on the surface, which tends to smear out the heat-capacity anomaly and (ii) an obvious reduction in signal size due to a decreasing presence of liquid H_2 in the system. This will make the signal hard to detect in heat-capacity measurements. Both effects are also reflected in our measurements, as the hysteresis effect occurs over a much broader temperature interval and decreases in size. There is only overlapping of the cooling and the heating curve when all the H_2 molecules are frozen, as at 6.4 K for 33% filling in Fig. 11. For 17%, this temperature is even lower.

This leaves the possibility for the presence of liquid H_2 at lower temperatures than known so far. The small pores to fill first will be on the small side of the pore size distribution (strongest adsorption potentials) and these should have the lowest freezing temperatures. This makes that liquid H_2 may still be present in the Vycor, not in the form of a bulk system or of a full layer, but as islands or strands in the Vycor pores. This is not in contrast with the less than a monolayer filling fraction, as the simultaneous growth of a bilayer of H_2 molecules in the system was observed. Similar reduction of the freezing temperature for subsequent layers of adsorbed molecules has already been detected for H_2 absorbed on MgO substrates.[27,28]

V. CONCLUSION AND FINAL COMMENTS

In this paper, we applied the potential of Raman scattering to perform microscopic measurements on molecules adsorbed on a surface or confined in a porous material on a particular case of H_2 in Vycor. We were able to separate signals from the molecules directly adsorbed on the surface (or possibly in the second layer) and to follow the adsorption process for very small amounts of H_2 molecules. Our microscopic measurements provide complementary results to heat-capacity experiments, as e.g., the different results obtained using different cooling rates. Our Raman data show that for sufficiently slow cooling rates the molecules are able to orient into an ordered structure, while for faster cooled systems, the molecules freeze into a probably glassy state.

Our results indicate that there still remains a possibility to supercool H_2 liquid down to temperatures which are of the order of the predictions for a superfluid transition to occur. These molecules probably correspond to the small islands of H_2 on top of first layer. A small quantity of these molecules will be hard to investigate and the reduced mobility of the liquid will make it difficult to detect it. Probably other means of supercooling H_2 are more promising.

Our results provide an interesting asset for computer calculations which may model the surface potential and provide more information about discrete interaction sites, island formation and the mobility of the H_2 molecules in the adsorbed state.

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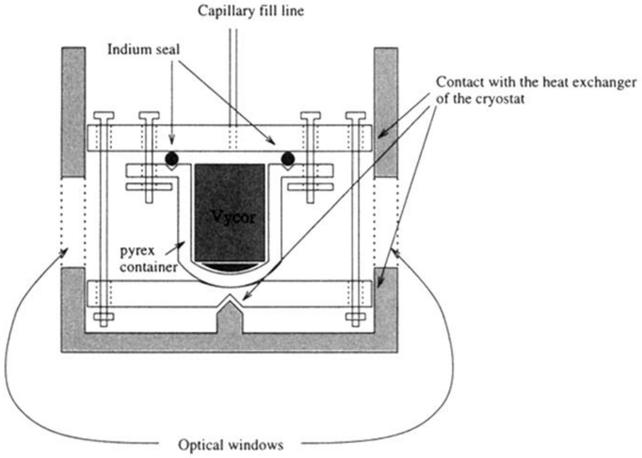

FIG. 1. Cross section of the mounting of the Vycor material in the interior part of a helium flow cryostat suitable for optical spectroscopy. The whole setup has, apart from the three optical windows and the fixing screws, a cylindrical symmetry around the fill line.