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Rotational dynamics of n-H_2 in porous Vycor glass

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The rotational kinematics of normal H_2 confined to the pores of Vycor glass have been studied via incoherent inelastic neutron spectroscopy. At low temperature we observe two distinct rotational transitions. One is centered near 14 meV, corresponding to the free rotor value of molecular H_2, while the other is centered at ~10 meV. Measurements taken at filling fractions ranging from 10% to 95% allow us to ascribe the two transitions to H_2 in the center of the pore and H_2 strongly bound to the pore surface, respectively. The molecules bound to the surface are modeled as rotationally hindered rotors, and a distribution of orientation-dependent interaction potentials is extracted. The bound molecules can further be divided into a monolayer that is in direct contact with the pore wall, and a second, less tightly bound layer. The ortho to para conversion rate has also been measured and is higher than the bulk rate of 1.9%/h. The rate for the molecules bound to the pore wall is 2.1%/h, while the rate for molecules in the center of the pore is 8.5%/h. [S0163-1829(99)03920-X]

I. INTRODUCTION

Recently, there has been a great deal of interest in the adsorption of simple materials in porous media. The physisorption of molecules on surfaces is particularly interesting as the effect of the interaction with the surface on the rotation of the molecule may be investigated. Molecular hydrogen is an attractive system to study in this regard. Due to its light mass and weak electronic interactions, molecular hydrogen is well described as a quantum rigid rotor with discrete energy levels characterized by the rotational quantum number J. Furthermore, the small moment of inertia of the molecule leads to a large energy level spacing which significantly simplifies experimental studies. Thus in the last half century the rotational behavior of H_2 adsorbed onto surfaces has been studied extensively,[1–4] in the hope that one could gain an understanding not only of the interaction of the H_2 with the surface, but also learn about and possibly characterize the surface itself. Much work has been undertaken recently concerning H_2 on the surface of Vycor, as it is a prototypical mesoporous material, and a significant amount of data exists in the literature.[5–10]

Hydrogen nuclei are fermions and, when confined in a molecule, can be separated into two species based on the symmetry of the spatial and spin wave functions, ortho (o-H_2) and para (p-H_2), with the para species having a slightly lower energy due to the symmetry of its rotational wave function. At room temperature, the energy separation between the rotational energy levels is relatively small, and the odd and even rotational states are populated in a 3:1 ratio in normal (n-H_2) utilized in this study. Upon condensation, the conversion of the o-H_2 to p-H_2, which requires a magnetic-field gradient, is relatively slow (on the order of several days) allowing the o-H_2 molecules to be studied as a stable impurity.

In the liquid and high temperature solid ($T > 3$ K) the molecules are well described as isotropic rigid rotors with the rotational energy levels given by

$$E_J = BJ(J+1), \tag{1}$$

where B is the rotational constant which is equal to 7.35 meV for H_2, and 3.70 meV for D_2.[4] Thus the rotational energies of the o-H_2 ($J=1$) and p-H_2 ($J=0$) states are 14.7 and 0 meV, respectively. Note that since the molecules behave as isotropic rotors, the energy is independent of the z component of the angular momentum m_J.

It is known that adsorption of molecules onto surfaces can alter their rotational behavior.[5,11,12] An orientation-dependent interaction with the surface can hinder the rotational motion of a nonspherical molecule, such as o-H_2, leading to shifts and splitting of the rotational energy levels.[5] Silvera, for example, found that H_2 adsorbed on grafoil had the same rotational transition energy as bulk H_2, while the transition energy was cut in half by adsorption on activated alumina.[4] The orientation-dependent interaction at the surface also introduces a preferential adsorption of one rotational state of the molecule onto the surface. Sandler[2] first noticed that the o-H_2 concentration of H_2 desorbed from a TiO_2 surface was greater than the gas above the surface. Preferential adsorption of the o-H_2 has also been observed on leached glass[1] and activated alumina.[13] White and Lassettre presented a theoretical treatment of the relationship between the rotational hindering potential and the preferential adsorption of the o-H_2 species.[3]

The transition of an o-H_2 to the para state can be induced by the interaction of the molecule with the magnetic moment of a neutron. The neutron gains the energy released by the H_2 molecule in the transition. At low temperature, all other modes which could donate energy to the neutron, such as phonons, are rapidly frozen out. Consequently, inelastic incoherent neutron spectroscopy (IINS) measurements, executed in neutron energy gain, are uniquely suited to probe the o-H_2 to p-H_2 transition, without interference from other processes.

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We report the results of IINS studies of H_2 and D_2 in Vycor, which directly probe the effects of adsorption on the rotational transitions of the adsorbates. Porous Vycor glass has been used extensively in studies of surface interactions due to its large interfacial pore surface area ($\sim$200 m^2/g), and is well characterized.[10,14,15] Typically, a single monolayer is strongly bound to the pore wall, while additional atoms adsorbed in the pores interact only weakly with the pore wall. Normal H_2 (n-H_2), however, forms a bilayer that is strongly adsorbed onto the Vycor pore wall.[16]

Our studies observe two peaks in the inelastic neutron-scattering spectra associated with two distinct states in the confined solid: a bulklike state in the center of the pores, and a rotationally hindered surface state. The surface state may be further divided into first and second layers, with the first layer ''feeling'' a stronger perturbation from the pore wall. By monitoring the amplitude of the two peaks with respect to time we determine that the ortho to para relaxation rate of H_2 confined in Vycor is much more rapid than in the bulk.

II. EXPERIMENTAL DETAILS

The porous medium used in these studies was commercially available porous Vycor glass. Vycor is produced by spinodal decomposition of a borosilicate glass followed by leaching of the boron-rich phase to produce an interconnected network of pores with a nominal radius of 35 Å.[14] The sample used in this measurement was in the form of a rod 60 mm long, with a diameter of 14 mm. The rod was split into ten thin disks to facilitate cleaning which was carried out by boiling in a 30% hydrogen peroxide solution. The sample was then rinsed in acetone, isopropyl alcohol, and distilled water followed by drying at an elevated temperature in a dry nitrogen atmosphere. The clean Vycor was then transferred to a tight-fitting thin-walled Al cell.

The cell was mounted in a helium ''flow'' cryostat modified to reduce background scattering from the Al tails. Silicon diode thermometers on both the cell and the heat exchanger of the cryostat monitored the sample temperature. Standard volumetric techniques were used to slowly condense measured amounts of n-H_2 into the cell through a heated stainless-steel fill line. The fill line heater was switched off on completion of the filling procedure to further avoid thermal gradients across the cell.

Measurements were carried out at a variety of pore fillings. We define the filling fraction f as the ratio of the number of moles adsorbed in the Vycor to the number of moles needed to completely fill the pores. Filling fractions of 0.10, 0.20, 0.27, 0.32, 0.45, 0.55, 0.65, 0.75, 0.85, and 0.92 were investigated in this study. Following the completion of a measurement on a given filling fraction, the cell was warmed to roughly 100 K and evacuated to remove residual H_2 before continuing to the ensuing filling fraction. This procedure provided a well defined o-H_2 concentration at the beginning of each measurement, and avoided loss of signal due to the ortho-para conversion of H_2 in the pores. The count time of the neutron-scattering measurements varied for different filling fractions, from 1 h at the higher filling fractions to 4 h at $f=0.10$.

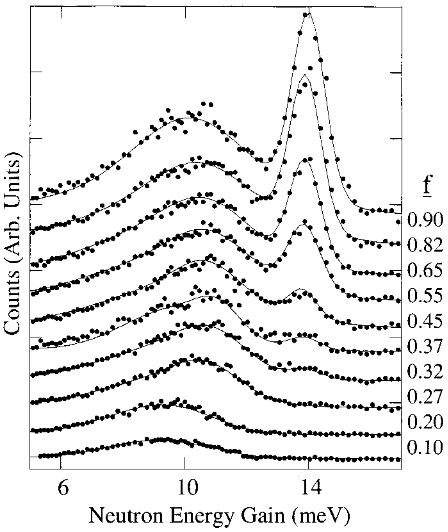

FIG. 1. IINS spectra of H_2 in Vycor at various pore-filling fractions at 5 K. The filling fraction, as defined in the text, is shown at the right of the figure. The solid lines are guides to the eye.

The inelastic scattering spectra were collected on the time-of-flight Fermi chopper spectrometer at the NIST National Center for Neutron Research. The incident cold neutron beam was monochromated by double Bragg reflection from two pyrolitic graphite (002) crystals. The monochromatic beam, $\lambda=4.8$ Å, impinging on the sample was scattered onto the detectors 2.27 m from the sample which covered an angular range from 5° to 135°. The inelastic measurements were executed in neutron energy gain mode because all collective processes are frozen out at low temperature, leaving a minimal background on the neutron energy-gain side. The instrumental resolution of the spectrometer at high-energy gain increases roughly linearly with energy leading to a resolution of $\sim$1.5-meV full width at half maximum at an energy gain of 15 meV.

Inelastic neutron-scattering spectra were collected at a variety of temperatures and fillings. The data were summed from detectors corresponding to momentum transfers of 0.6–1.6 Å to decrease statistical uncertainty. This presents no problems for the study of the rotational transitions, which are dispersionless.

III. EXPERIMENTAL RESULTS

Figure 1 shows the inelastic neutron-scattering spectra of solid H_2 confined in Vycor glass at 6 K at several different fillings. For filling fractions below $f=0.45$ only a single peak in the scattering is present which has a width significantly greater than the instrumental resolution. At higher fillings, a second peak, with a width comparable to the instrumental resolution, appears. The locations and areas of these peaks have been extracted by fitting them with a sum of Gaussians, and are shown in Fig. 2.

As can be seen in Figs. 1 and 2, at low filling fractions, $f\leqslant 0.20$, a single broad peak, with an intensity that approximately scales with the filling fraction, is observed at a neutron energy gain of 9.1 meV. The peak shifts to an energy gain of 10.1 meV between filling fractions of 0.20 and 0.27. This shift in the peak center corresponds to completion of the first monolayer on the pore surface. The peak location is relatively constant, while its intensity continues to increase

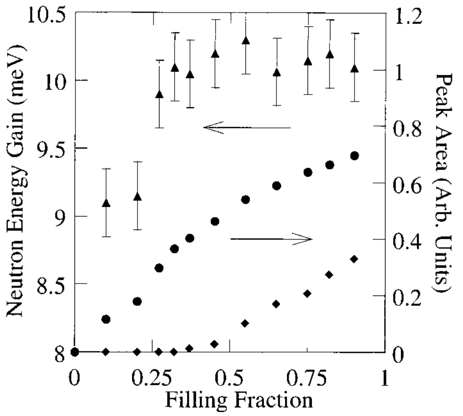

FIG. 2. Area and center of the inelastic peaks as a function of pore filling as determined by Gaussian fits to the peaks. The filled circles (●) give the area, and the filled triangles (▲) the location of the broad peak. The filled diamonds (◆) give the area of the narrow peak at 14 meV. The location of this peak does not change with filling, and has not been shown.

approximately linearly with the filling fraction until $f=0.45$. At $f=0.45$ a small peak appears at 14 meV. Above $f=0.45$ the peak at 14 meV, which has a width comparable to the instrumental resolution, becomes increasingly intense. The broad peak at 10.1 meV continues to grow in intensity with filling, albeit at a reduced rate, to the highest filling fractions studied. Note that at all filling fractions above 0.45 the two peaks are easily resolvable.

Figure 3 shows the IINS spectra of H_2 in Vycor with full pores at temperatures corresponding to the bulk liquid (16 K) and solid (8 K) phases. The peaks at neutron energy gains of 14 and 10 meV are present in both phases. The inelastic peaks are distinct at low temperature. At high temperature, in the bulk liquid phase, the elastic and 14-meV peaks are broadened significantly due to contributions to the scattering from diffusing molecules. In contrast, the peak at 10 meV is relatively unaffected by the phase change, neither in amplitude nor width. This indicates that, in the temperature range of the bulk liquid phase, the sample associated with the broad peak is nondiffusive, i.e., solid.

At low filling fractions, only the peak at 10 meV is present. This observation, coupled with the temperature independence of this component of the scattering, allows us to associate this scattering with a adsorbed layer of H_2 strongly bound to the pore surface. The appearance of scattering at 14 meV, corresponding to the free molecule transition, for fillings above 0.45 is associated with the appearance of ‘‘bulk-like’’ material in the pore center. The clear separation of the scattering from molecules adsorbed on the walls and in the pore center suggests that these are quite distinct states. Henceforth, we shall refer to these as the bound and bulklike states, respectively. We shall defer a detailed consideration of the amount of material in each of these states until later.

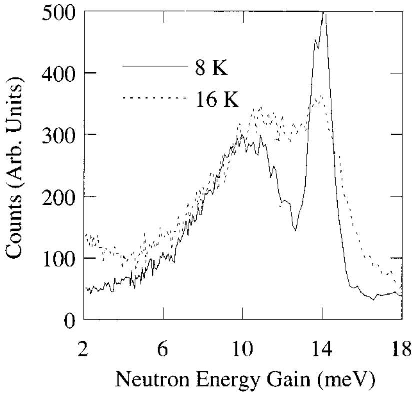

FIG. 3. IINS spectra of confined H_2 at 8 (solid) and 16 K (liquid) for a pore filling of 0.90.

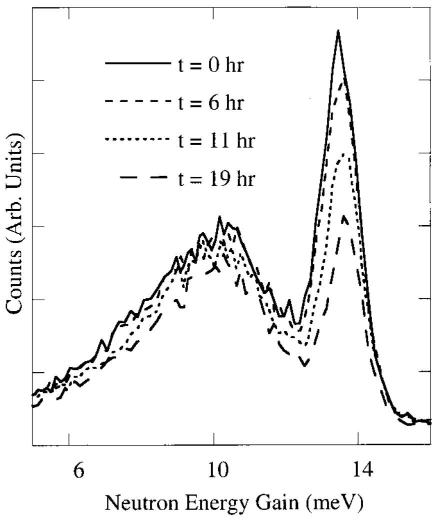

FIG. 4. IINS spectra of confined H_2 as a function of time.

The peaks in the IINS spectra of H_2 confined to Vycor are the result of incident neutrons gaining the energy released in an o-H_2 to p-H_2 transition. As such, the intensity of the peaks is proportional to the amount of o-H_2 present in the sample at a given time. At low temperatures in the bulk, o-H_2 is known to slowly (over a period of several days) convert to the p-H_2 state due to interactions among the molecules. It is important to note that the neutron-stimulated conversion is negligible compared to this intrinsic rate. Figure 4 shows the IINS spectra of confined H_2 as a function of time. The conversion of o-H_2 to p-H_2 is manifested by the reduction of the intensity of the peaks with time. It is evident that while both peak intensities decrease with time, the bulklike peak diminishes more rapidly.

We have also measured the scattering from D_2 in Vycor with complete pore filling. D_2 is nearly identical to H_2 in terms of its electronic configuration, while having a rotational constant B which is half that of H_2, due to the difference in nuclear mass. Thus the free rotational transitions in D_2 will occur at half the energy of in H_2. However, if the energy is scaled by B, the free rotational transitions will occur at the same location. Figure 5 shows the scattering from both D_2 and H_2 at full pore filling as a function of E/B. As expected, the narrow peaks we attributed to the molecules in the center of the pore both occur at $E/B=2$, further confirming our identification of the narrow peak as originating from bulklike material in the pore center that behaves as free rotors.

The broad peaks which we associate with scattering from molecules adsorbed on the pore walls, however, do not occur at the same location on this reduced energy scale. The bound

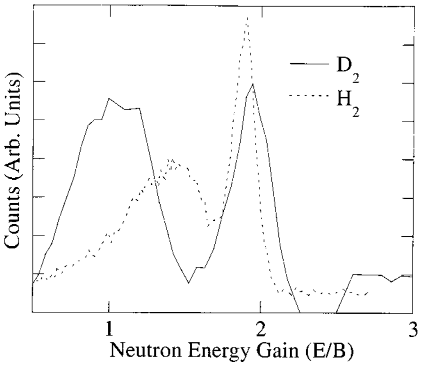

FIG. 5. IINS spectra from confined D_2 (solid line) and H_2 (dotted line) plotted vs the energy transfer relative to the rotational constant.

peak of D_2 is at $E/B_D = 1.0$, and that of H_2 is at $E/B_H = 1.36$. This is to be expected if the energies of the peaks are strongly influenced by interactions with the pore surface. The interactions of D_2 molecules with the pore wall should be similar to those of H_2, because the spatial distributions of the electrons in the molecules, which will determine the interaction with the surface, are nearly identical. However, there is no reason for these interactions to scale directly with B. Therefore, the locations of the bound peaks would not be expected to occur at the same location for H_2 and D_2 when plotted versus E/B.

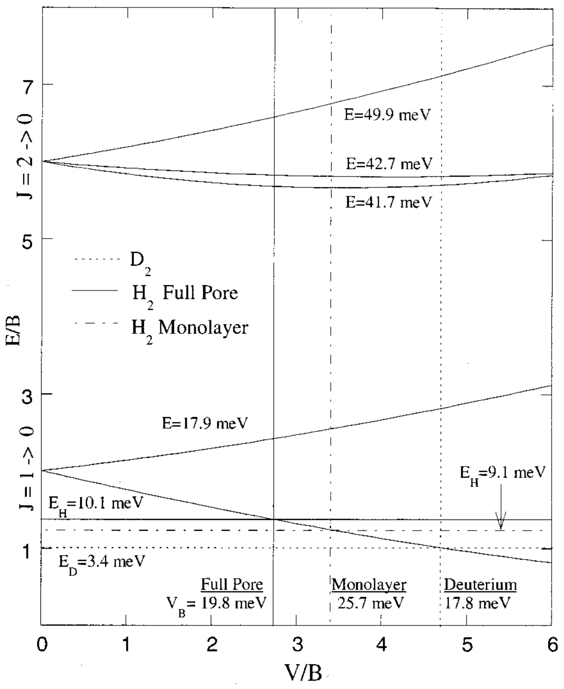

FIG. 6. Shift of the rotational energy levels of H_2 as a function of barrier height. The vertical solid line is the inferred rotational barrier for H_2 in Vycor for the second layer. The dash-dotted line shows the rotational barrier for the first adsorbed monolayer. The dotted lines show the rotational potential for deuterium.

IV. DISCUSSION

A. Rotational hindering potential

We first consider the high filling data where the scattering exhibits a broad peak at 10 meV and a sharp peak at 14 meV. We have argued above that the sharp component is due to neutron-stimulated ortho-para conversion of H_2 molecules in the center of the pores behaving as free rigid rotors. This behavior has been observed in the bulk where the rotational transitions have been extensively studied.[4] The sharp peak we observe in the scattering occurs at a neutron energy gain of 14.0 meV, rather than the predicted value of 14.7 meV. This shift of the rotational energy levels has been observed in previous studies of the rotational transition in bulk H_2 with high ortho concentrations.[17] The shift is due to ortho-ortho interactions that slightly modify the energies of the rotational transitions and is consistent with the shift that we observe.

The full pore scattering shown in Fig. 1 also exhibits a broad component centered at ~10 meV. This component appears when H_2 is first admitted to the cell and grows in intensity as the filling is increased, rapidly at first and then more slowly as the pore fills. Since this broad peak appears immediately upon admission of H_2, we have argued that it is associated with molecules strongly bound to the pore wall. The temperature-dependent data of Fig. 3 also supports this assignment. The broad peak is essentially independent of temperature as expected for molecules strongly bound to the surface.

White and Lassettre[3] considered the rotational energy levels of H_2 interacting with a surface via a potential that depends on the distance from the surface, z, and the azimuthal angle between the molecular axis and the surface. Symmetry considerations require the potential to be a function of $\cos^2\theta$, $V = V(z, \cos^2\theta)$, which can be expressed in a Taylor expansion about the equilibrium position and angle. This yields an interaction of the form $V_s = V_0 + C\cos^2(\theta) + K(z - z_0)^2 + \cdots$, where V_0, C, and K are constants.[3]

The Schrödinger equation remains separable into translational and orientational components when only the leading order terms of this expansion are maintained. The orientational component of the Schrödinger equation may be solved treating the orientational potential as a perturbation. It is most convenient to express the orientational potential as $V = V_B(1 - \cos 2\theta)$, where V_B is the classical barrier to rotation,[18] and to solve the Schrödinger equation perturbatively to second order by an expansion of the potential in the wave functions of the unperturbed H_2 molecule, i.e., the spherical harmonics. The resultant matrix is diagonalized numerically to determine the rotational energy states of the surface molecules. We have truncated the expansion after 49 levels, yielding an accuracy on the order of $10^{-4}B$. The calculated transition energies, normalized to B, are plotted as a function of the barrier height in Fig. 6. The levels continue to be referred to by the quantum number J, even though J may no longer be a good quantum number. Note that the perturbation has split the m_J sub-levels of the $J=1$ and 2 states.

The broad component of the scattering from hydrogen in Fig. 5 located at $E/B_H = 1.37$ corresponds to an orientational potential barrier with a strength of $V_B/B_H = 2.7$ ($V_B = 19.8\,\mathrm{meV}$). Likewise, for D_2, the peak of the broad component occurs at $E/B_D = 1.0$, corresponding to $V_B/B_D = 4.8$ ($V_B = 17.8\,\mathrm{meV}$). The potential barriers determined for H_2

and D_2 are in reasonable agreement, as expected since the spatial distribution of the electron cloud of the isotopes are nearly identical. The magnitude of this orientational potential is quite large, comparable to that seen in alpha alumina, a catalyst used for o-H_2 enrichment.[4] Similar results have also been inferred for H_2 adsorbed on leached glass.[1]

At filling fractions below 1 ML, the broad peak is centered at a neutron energy gain of 9.1 meV. Using Fig. 6, we determine that this energy shift corresponds to a barrier height of 25.7 meV for the first monolayer. The energy of the $J=0-2$ rotational transition of the H_2 in contact with the surface may also be determined from Fig. 6. Again, the m_J sublevels are split by the perturbation. Using the inferred barrier height of 25.7 meV, the $J=0-2$ transition energies are predicted to be 41.7, 42.7, and 49.9 meV, as compared to the bulk transition energy of 44.1 meV. The $J=0-2$ transition is not observable in this measurement, but has been measured in previous Raman scattering studies. DeKinder, Bouwen, and Schoemaker studied the rotational behavior of p-H_2 in Vycor at filling fractions less than 1 ML.[5] At filling fractions less that 0.20, transitions were observed at 40.4, 41.3, and 47.6 meV, in reasonable agreement with our simple model.

B. Origin of the surface orientational potential

The potential barrier to rotation observed in this study is quite large. It is at least an order of magnitude larger than has been seen for H_2 on a smooth surface, such as grafoil.[13] There are several possible origins of the orientational potential observed in this study. Studies of the pore surface of Vycor have indicated the presence of individual OH groups, which are removed upon heating about 190 °C, as well as small (~17 Å) strongly chemisorbed clusters of water molecules. It is possible that the charge state associated with these molecules effects the rotational behavior of the adsorbed H_2 molecules. However, one would expect that such surface impurities would create orientational potentials that varied from zero far from the cluster to a large value near the cluster. The relatively narrow scattering associated with the hindered rotors, therefore, argues against this.

A second possible origin for the large orientational potential is the atomic scale surface roughness of the pore walls of Vycor. It is believed that the surface of Vycor demonstrates fractal roughness on the atomic level which has been attributed to silica bonds dangling from the pore surface.[15] The addition of a monolayer of adsorbate may reduce the surface roughness considerably, whereas several layers might completely conceal the surface roughness.

To explore the effect of surface roughness we have carried out a molecular dynamics simulation of the rotational dynamics of a single hydrogen molecule adsorbed onto smooth and rough surfaces. In the case of a smooth surface, the H_2 molecule is above the (100) plane of a simple cubic pore wall, with a number density equal to that of SiO_2. The rough surface is created by adding a displacement d_i to the position of the ith atom of the crystalline surface. The displacements d_i are chosen randomly, but are constrained to have roughly a Gaussian distribution centered at zero with full width at half maximum of approximately 25% of the atomic spacing. In both cases, the glass molecules are treated as single particles interacting with the hydrogen atoms through a Lennard-Jones potential with $\varepsilon=200\,\mathrm{K}$ and $\sigma=3.32\,\text{Å}$.[10]

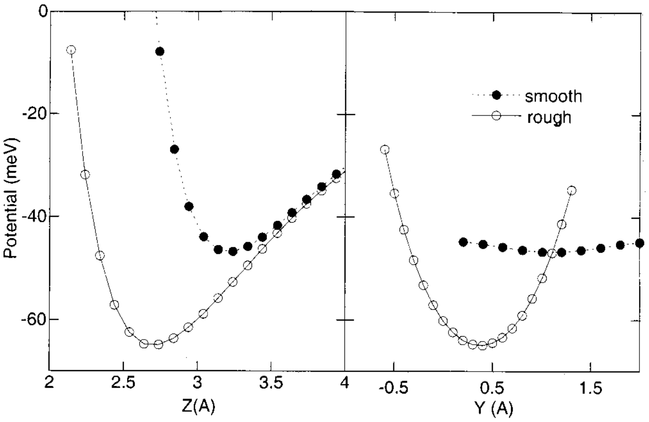

FIG. 7. Potential energy of a H_2 molecule as a function of the distance above (z) and translation across (y) simulated smooth and rough surfaces.

The simulation was carried out by placing the molecule at a random position above the surface, and allowing it to move until it finds a local minimum in the potential. Figure 7 shows the adsorption potential near the minimum as a function of distance above (z) and across the surface (y) for both the smooth and rough surfaces.

The simulated potentials may be compared to the experimental results obtained in Ref. 10 through heat-capacity and isothermal adsorption measurements of H_2 in Vycor. They measured the binding energy of H_2 on Vycor to be 46.6 meV, in qualitative agreement with the depth of the potential wells shown in Fig. 7. The rough surface, however, provides a much stronger confinement of the lateral movement of the molecule than does the smooth surface, as would be expected.

The vibrational frequency of the molecules in the z direction is determined from the curvature of the potential function near the minimum to be $\hbar\omega=17.4$ meV. Assuming a Lennard-Jones interaction between the silica particles and H_2 molecules, the authors of Ref. 10 also estimated the vibrational frequency of the H_2 molecules in the attractive field of the surface to be roughly $\hbar\omega=22.4\,\mathrm{meV}$. Wang and Sokol[19] extracted a similar value of 17.3 meV from deep inelastic neutron-scattering measurements of H_2 in Vycor.

Figure 8 shows the potential ''felt'' by the H_2 molecule on the smooth and rough surface as a function of the azimuthal (ϕ) and polar (θ) angles of the molecular axis. While the potentials are not strictly sinusoidal as in the model of Ref. 3, it is plausible that when averaged over the entire surface the average potential will approximate that used in Ref. 3. In the case of the smooth surface, the potential barrier to rotation is small, i.e., $V_B<1\,\mathrm{meV}$. A more substantial barrier to rotation, ~11 meV, exists if the H_2 molecule is held above a rough surface, as shown in Fig. 8. The rotational barrier above the rough surface is of the same order of magnitude as that observed for a H_2 molecule on Vycor in this study.

This suggests that disorder, e.g., a surface which is rough on an atomic scale, is responsible for the strong perturbation of the rotational wave functions. Indeed, Silvera and

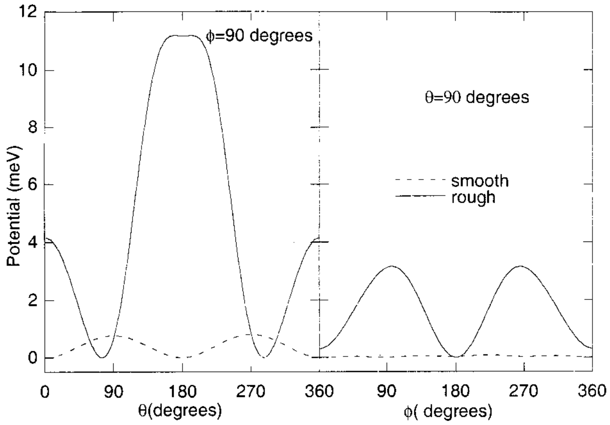

FIG. 8. Potential ''felt'' by H_2 molecules as a function of azimuthal angle (θ) and polar angle (ϕ) above simulated smooth and rough surfaces.

Nielsen[13] found no energy shift in their study of H_2 on grapfoil, which has a smooth surface on an atomic scale. Thus, the results of this experiment may be indication of the surface roughness of Vycor, which has been debated recently.[14,20,21] The large shift of the rotational energy levels reported here is consistent with pore walls that are rough on an atomic scale. However, they also suggest that the theory of White and Lassettre[3] may be an oversimplification of this case, as it ignores hindrances to the rotation in the plane parallel to the surface (polar rotations).

C. Selective adsorption

The observed rotational transition energies of bound layers of H_2 in Vycor agree well with a model of an orientation-dependent interaction hindering the rotation of the H_2 molecule. This anisotropic adsorption potential reduces the free energy of the odd rotational states of molecules on the pore surface relative to the even states,[22] leading to a preferential adsorption of o-H_2 on the pore surface. The separation factor describes the extent to which o-H_2 is preferentially adsorbed, and is defined as

$$S=\frac{(\rho_o/\rho_p)_{\mathrm{bound}}}{(\rho_o/\rho_p)_{\mathrm{bulklike}}}, \tag{2}$$

where $(\rho_o/\rho_p)_{\mathrm{bound}}$ and $(\rho_o/\rho_p)_{\mathrm{bulklike}}$ are the molar ratios of o-H_2 to p-H_2 states in the bound and bulklike phases, respectively.[3,13] In normal H_2 at room temperature and in liquid n-H_2 directly after condensation, $(\rho_o/\rho_p)=3$, which simply reflects the equal occupation of the $J=0$ and 1 states at room temperature.

For the adsorbed molecules, $(\rho_o/\rho_p)_{\mathrm{bound}}$ may be calculated from the partition functions of the o-H_2 and p-H_2 states in the presence of the surface potential. The translational and vibrational energy levels are equivalent for the ortho and para states. Assuming the variables are separable, the separation factor simplifies to the ratio of the rotational partition functions.[13] At low temperature only the $J=0$ and 1 states are populated and need be considered. The separation factor may then be written as

$$S=\frac{1}{3}\exp\left[\frac{(2B-\Delta_0)}{kT}\right]+\frac{2}{3}\exp\left[\frac{(2B-\Delta_1)}{kT}\right], \tag{3}$$

where Δ_0 and Δ_1 are the energies of the $J=1$ and $m=0$ and 1 sublevels relative to the ground state, i.e., $J=0$.[13]

The values for Δ_0 and Δ_1 can be determined from the energy-level diagram shown in Fig. 6, giving $\Delta_0 = 10.1$ meV and $\Delta_1 = 17.9$ meV. The separation factor increases rapidly with decreasing temperature and, at 6 K, where these measurements were carried out, the separation factor is greater than 1000. Thus, the o-H_2 concentration of the bound state is near 100% when excess o-H_2 is available to the surface. If the barrier height is not temperature dependent, the separation factor would be 4.5 at 20.4 K, comparable to the calculations of White and Lassettre,[3] but somewhat smaller than that found by Silvera and Nielsen[13] on alumina. While the separation factor is strongly temperature dependent, the ortho concentration of the surface layer only varies from roughly 94% to essentially 100% between 20 and 6 K. Thus, on loading, a significant amount of o-H_2 will not be present in the bulklike state until the bound state is completely saturated.

D. Filling dependence of the rotational energy levels

Inelastic neutron-scattering spectra from the bulklike and bound states of H_2 in Vycor are shown in Fig. 1 at various filling fractions from 10% to nearly full pores. As discussed earlier, the broad peak that appears at low filling is identified with molecules adsorbed onto the pore surface, which experience a strong orientational potential. The bound state may be further separated into a layer that is in direct contact with the pore wall, and a second layer that feels a relatively weaker orientational potential.

The scattering from the first and second layers can be separately determined if we assume that the intensity of the scattering from the first layer varies linearly with filling up to layer completion. Figure 9 shows the scattering from a single monolayer of adsorbed H_2 ($f\sim0.25$) as well as from slightly more that two layers ($f=0.45$). At the higher filling the bulklike peak is just becoming apparent. The scattering from the second surface layer and above is obtained from the difference of these two spectra, and is also shown. This difference is fit with the sum of the bulklike peak, determined previously (Fig. 1), and a single Gaussian, which represents the scattering from the second adsorbed layer. The scattering from the second layer is centered at $E=11.3$ meV, compared to the first layer which is centered at 9.1 meV. This shift in energy indicates that the second layer perceives less of a perturbation from the wall then does the first.

The width of the peak we associate with the bulklike molecules is due entirely to instrumental resolution. This is consistent with the view of these molecules as being free rotors with a single well defined value for B. On the other hand, the width of the peak which we attribute to the bound layer is much broader than the instrumental resolution. A single well-defined orientational potential would yield a shift in the peak location, as observed, but no additional broadening, since the energy levels would still be well defined. Thus we attribute this additional width to a distribution of orientational potentials. This is not surprising considering the inho-

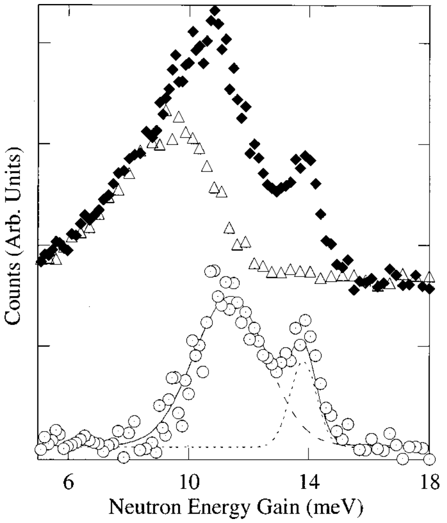

FIG. 9. Scattering from a monolayer (◆) and $f=0.45\cdot(\triangle)$, slightly more than a bilayer of H_2. The difference of the two is shown by (○), representing scattering from the second layer and slightly higher. The solid line represents the fit to the difference curve, with the components of that fit being the dotted (bulklike peak) and dashed (second layer) lines.

mogeneous pore surface of Vycor. The distribution of the orientational surface potentials can be directly extracted using the model of White and Lassettre[3] to describe the shifts of the rotational energy. The strength of the scattering, when the instrumental resolution is removed, at a given energy is directly proportional to the number of molecules with that orientational potential. Thus, plotting the resolution corrected scattering as a function of V/B_H, obtained from Fig. 6, directly gives the distribution of orientational potentials, as shown in Fig. 10.

As can be seen, the orientational potential for the first layer is broad, asymmetric, and centered at $V_B=3.5B_H=25.7$ meV, whereas the orientational potential of the second layer is relatively narrow and centered at $V_B=2.0B_H=14.7$ meV, indicating a weaker interaction with the surface. This is in agreement with the picture presented by Katsaros *et al.*,[15] in which the roughness is created by dangling bonds on the pore surface. The presence of a monolayer of H_2 on the surface reduces the effect of these dangling bonds which are buried, to some degree, by the adsorbate. The second layer subsequently senses a weaker orientational interaction with the pore surface. The measured potential strengths are of the same order as the orientational potential found for H_2 on a leached glass surface.[1]

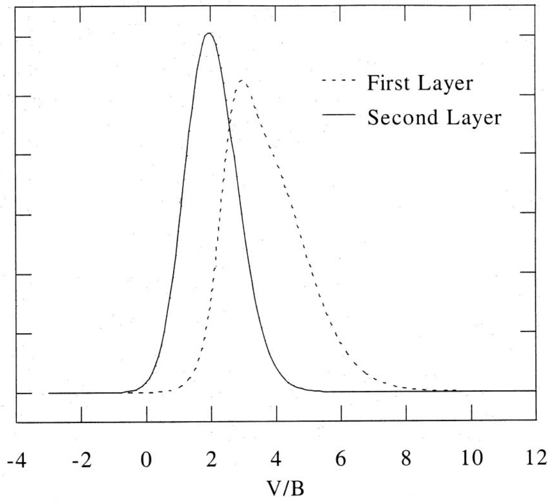

FIG. 10. Distribution of potential barriers felt by the molecules in the first (dashed line) and second (solid line) layers.

Figure 2 shows the amplitude of the bound and bulklike peaks as well as the location of the bound peak as a function of filling. The intensity of the bound peak, at low fill fractions, is linear with filling. The bulklike peak is just visible at $f=0.32$ and 0.37, indicating that a small fraction of the o-H_2 molecules have entered the bulklike state. Ortho molecules begin to significantly populate the bulklike state at $f=0.45$, as seen in Fig. 2. Above $f=0.45$ the bulklike peak grows linearly with increased filling. Unexpectedly, the bound peak also continues to grow slowly above $f=0.45$, indicating that increased filling drives more H_2 into the bound state.

Huber and Huber[16] demonstrated, through molecular adsorption measurements, that a bilayer of H_2 is adsorbed onto the pore wall at low temperature and pressure. This bilayer accounts for ~33% of the adsorbed H_2 when the pores are full. The bound state observed in this study may be identified with that bilayer. At filling fractions of less than 0.33, the preferential adsorption of the o-H_2 species is of no consequence, as all of the sample will be adsorbed regardless of which species is preferred. However, above $f=0.33$, o-H_2 will begin to displace p-H_2 from the bilayer, and p-H_2 will begin to exist in the bulklike state. Unfortunately, the incident neutron energy in this measurement is not enough to excite a p-H_2 to o-H_2 transition, and we are unable to observe this initial population of the bulklike state with p-H_2. The bulklike state will not be observed until the bound layer is completely filled with o-H_2 which occurs when $0.75f=0.33$ or, in other words, when the pores are approximately 44% full. Thus, the appearance of the bulklike peak at $f=0.45$ is in good agreement with the results of Huber and Huber,[16] i.e., that the bilayer is complete at $f=0.33$, and the assumption of a pure o-H_2 bilayer.

E. Ortho to para conversion of H_2 in Vycor

Ortho to para conversion of H_2 in the bulk arises from interactions of the nuclei of an o-H_2 molecule with the magnetic-field gradient of neighboring o-H_2 molecules. This gives rise to a bimolecular rate law for the ortho concentration c:

$$\frac{dc}{dt}=-Kc^2, \tag{4}$$

where K is the rate constant.[4] The time variation of the o-H_2 concentration for this rate law is easily obtained, and is given by

$$\frac{1}{c(t)}=\frac{1}{c_0}+Kt, \tag{5}$$

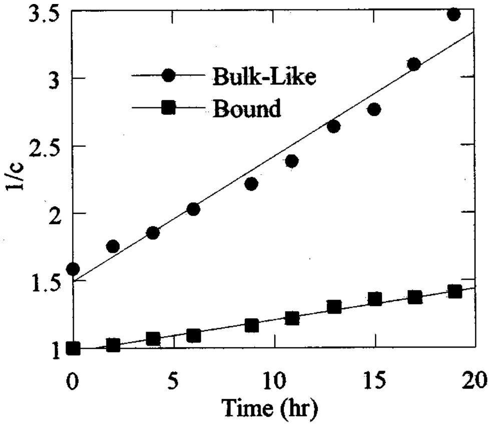

FIG. 11. Inverse of the o-H_2 concentration of the bound (■) and bulklike (●) states as a function of time. The slope of the fit lines yields ortho-para conversion rates of 2.1% and 8.5%/h for the bound and bulklike states, respectively.

where c_0 is the initial concentration. For bulk H_2 at saturated vapor pressure ($\rho_0 = 19\,\mathrm{cm}^3/\mathrm{mol}$), the rate constant is $K = 1.90\%/\mathrm{h}$.

The intensities of the observed signals in this measurement are directly proportional to the concentration of the o-H_2, and the conversion rate may be determined from the dependence of the peak intensities on time. In addition, the scattering from the bound and bulklike states are well separated in energy, allowing the conversion rate of each state to be determined independently. In these measurements, n-H_2, with an o-H_2 concentration of 75%, is condensed directly into the porous sample. However, as noted earlier, o-H_2 molecules are selectively adsorbed on the surface until the solid bilayer is saturated. Thus for a full pore sample the initial concentration of the bound states is 100% o-H_2, while the initial concentration of the bulklike states in the interior of the pore is 63%.

The bimolecular decay law obeyed in the bulk solid predicts that the inverse of the o-H_2 concentration, $c^{-1}(t)$, varies linearly with time. The inverse of the o-H_2 concentration for both the bound and the bulklike states is plotted as a function of time in Fig. 11 to highlight this bimolecular decay law. No attempt has been made to differentiate between the first and second solid layers when discussing the bound states. As can be seen, both bound and bulklike scatterings are in reasonable agreement with the predictions of a bimolecular decay rate. The rate constant, extracted from the slopes of the straight lines, is 2.1%/h for the bound states and 8.5%/h for the bulklike states. An enhancement of the conversion rate of H_2 in Vycor was noted by Beaudoin *et al.*[7] and eluded to by others.[23] However, to our knowledge this is the first quantitative measurement of the conversion rate of H_2 in Vycor. In addition, we believe this is the first measurement capable of extracting the conversion rate for molecules on the surface and in the pore centers separately.

The conversion rate in bulk H_2 is strongly dependant on the phonon density of states, since an energy of ~14 meV is released during the $J=1-0$ transition which must be adsorbed by lattice phonons. The density of states, and thus the conversion rate, is a function of the mass density of the condensed H_2. The conversion rate has been shown to reach a maximum of 6%/h at a density of $\sim 1.5\rho_0$, and then decrease with a further increase in density.[24]

The presence of the confining medium as well as effects of finite size (nearly one of four molecules are on the surface) could drastically change the phonon density of states of the confined solid. The change of the density of states of the confined solid may be the source of the rapid conversion of the confined o-H_2. Also, the density of states of the surface layer, which is likely to have an amorphous structure,[25] is almost certain to be different from that of the bulklike state. The density of states of the surface layer may even be significantly altered by the direct contact with the pore wall, perhaps mirroring the density of states of the substrate. Thus it is not surprising that the conversion of the H_2 in the bulklike and bound states are very different.

The extremely high conversion rate of the bulklike states is quite surprising. The measured rate of 8.5%/h is significantly larger than the maximum rate observed in the bulk solid (~6%/h) at high densities. Thus, a simple increase in the density of the confined liquid could not explain this result. In addition, this would be inconsistent with diffraction studies[8] that show the confined solid has a lattice spacing similar to the bulk. Another possibility is that localized modes exist at the boundary between the bulklike solid and the bound states, and that these localized modes are leading to enhanced conversion. Further theoretical and experimental studies are required to explore this question.

V. CONCLUSIONS

We have reported inelastic neutron-scattering studies of H_2 in porous Vycor glass as a function of filling fraction, temperature, and time. Our studies show that the H_2 exists in two distinct states in the pores; a bulklike state in the center of the pore, and a bound state on the pore surface. The molecules at the center of the pores behave like free rotors, as in the bulk, while the molecules bound to the surface, as hindered rotors. Measurements of D_2 in Vycor confirm this simple picture.

The rotational hindering of the bound molecules is due to an orientation-dependent interaction between the molecule and the pore wall. The magnitude of the orientational potential required to describe the observed scattering is quite large (~20 meV). This orientation-dependent interaction selectively adsorbs the ortho species of molecular hydrogen, so that the surface layers are nearly pure o-H_2. Through molecular-dynamics simulations we have shown that the large energy shift observed may be attributed to the surface roughness of the porous Vycor.

The bound state can be further divided into a first layer in direct contact with the pore wall, and a second which perceives less of a perturbation from the interaction with the pore wall. The distribution of the orientational potentials of these two layers has also been extracted. The potential for the first layer has a mean value of $3.5B_H$, and is very asymmetric. The potential for the second layer is smaller, $2B_H$ and much more symmetric.

The ortho to para conversion rate of both the bound and bulklike states has been measured and is significantly greater that the bulk conversion rate of 1.9%/h. The conversion rate for molecules in the bound state is 2.1%/h, which is consistent with a density in the bound state that is slightly larger than the bulk solid density. This enhanced bound density is to be expected in the presence of a strong adsorption potential. The conversion rate of the bulklike molecules in the center of the pore is 8.5%/h. This rate is much larger than the bulk, and cannot be understood in terms of any reasonable increase in the density of the solid. The origin of this enhanced conversion rate is unexplained at this time.

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