THE ROTATIONAL DYNAMICS OF H₂ IN POROUS VYCOR GLASS

Porous materials play an increasingly important role in the exploration of fundamental scientific issues related to diverse technological applications including adhesion, lubrication, tribology and the engineering of materials. Surface interactions and finite size effects both play a key role in the qualitative modification of the properties of the materials contained within the porous host. Due to its light mass and weak electronic interactions, molecular hydrogen is an ideal system to probe the effects of surface interactions. H_2 is well described as a quantum rigid rotor with discrete energy levels labeled by the rotational quantum number, J, and energies given by $E_J = BJ(J + 1)$ where B is the rotational constant which is equal to 7.35 meV for H_2. These energy levels can be studied by using neutrons to stimulate the J = 1 to J = 0 transition of the H_2 molecule, a process that is normally doubly forbidden due to the quantum statistics obeyed by H_2. When neutron stimulated conversion occurs, the neutron gains an amount of energy equal to the rotational energy of the molecule. This results in an extremely clean signal since all other processes are frozen out at the low temperatures of these measurements.

Studies of the rotational levels of H_2 adsorbed in Vycor, a commercially available porous glass, were carried out for pore fillings ranging from 0.10 (corresponding to less than a single monolayer on the pore surface) to 0.92 (corresponding to nearly full pores). As can be seen in Fig. 1, at low filling fractions only a single broad peak at 10 meV is present which can be attributed to the scattering from an 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 which we refer to as the bound and bulk-like states, respectively.

The shift in the energy of the rotational transition at low fillings can be directly related to the interaction of the molecules with the surface [2]. Figure 2 shows the shift of the J = 1 to J = 0 transition as a function of the rotational energy barrier for the molecule. From Fig. 2 one finds that the observed rotational energy of 10 meV corresponds to an orientational potential with a barrier height of $V_B/B_H = 2.7$ (V_B = 19.8 meV). The magnitude
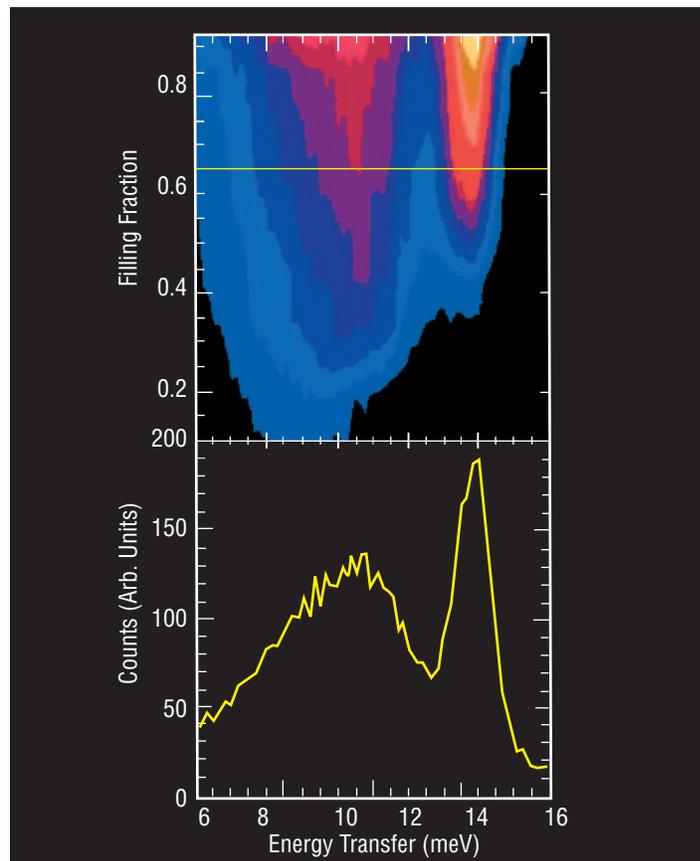

FIGURE 1. The top panel shows a contour plot of the inelastic scattering from H₂ in Vycor at various pore fillings at 6 K. The bottom panel is a cut through the contour plot at f = 0.65 (indicated by the line).

of this potential is quite large, comparable to that seen in alpha alumina, a catalyst used for ortho-H_2 enrichment [3], and on leached glass [4].

Careful inspection of the data reveals that the peak due to the bound state actually shifts from 9.1 meV to 10.1 meV between filling fractions, f, of 0.20 and 0.27. Thus for f between 0.27 and 0.45, the bound state may be separated into a layer in direct contact with the pore wall and a layer that feels a weaker orientational potential. The scattering from these two layers can be separately determined assuming the intensity from the first layer varies linearly with filling.

The scattering from the second surface layer can be obtained from the difference of the monolayer and bilayer spectra. The scattering from the second layer is centered at E = 11.3 meV, compared
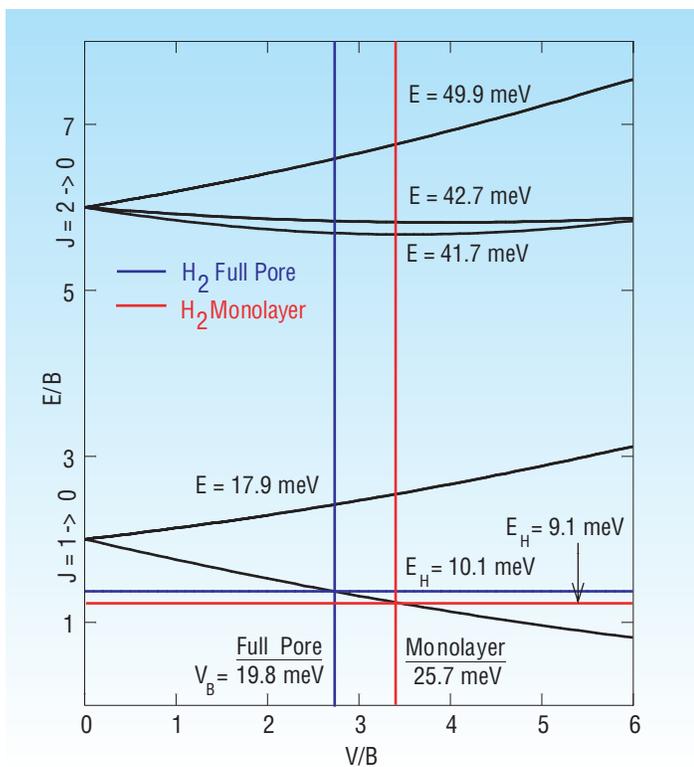
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FIGURE 2. Shift of the rotational energy levels of H_2 as a function of barrier height.

FIGURE 3. Distribution of potential barriers felt by the molecules in the first (red) and second (blue) layers.

to the first layer which is centered at 9.1 meV, indicating that the second layer interacts less strongly with the wall.

The width of the peak we associate with the bulk-like 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 which can also be directly extracted using the model of White and Lassettre [2] (Fig. 2). After correcting for instrumental effects, the strength of the scattering at a given energy is directly proportional to the number of molecules which feel the corresponding orientational potential. Thus, plotting the scattering as a function of V/B_H, directly yields the distribution of orientational potentials shown in Fig. 3. As can be seen, the
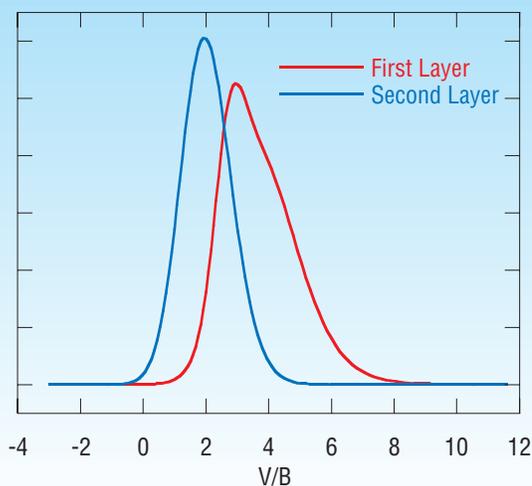
orientational potential for the first layer is broad, asymmetric, and centered at $V_B = 3.5B_H$, whereas the potential of the second layer is relatively narrow and centered at $V_B = 2.0B_H$, indicating a weaker interaction with the surface.

The data allow us to draw the following picture of the adsorption of molecular hydrogen on a porous glass surface. The first monolayer is bound tightly to the rough pore surface. The rough surface prevents free rotation of the molecule, altering the rotational energy states. The second layer perceives the surface roughness smoothed by the presence of the first layer, and accordingly, the rotational transitions are affected to a lesser degree. Subsequent to the completion of the second monolayer, the H_2 molecules sense no significant orientational interaction from the glass surface. This is in agreement with the picture presented by Katsaros et al. [5], in which surface roughness is created by dangling bonds on the pore surface.

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