Vibrational Spectroscopy of H_2 in Porous Vycor Glass: First Evidence for the Bilayer Structure

T. E. Huber and C. A. Huber

Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

(Received 18 July 1986; revised manuscript received 18 June 1987)

Infrared-absorption measurements have been performed on the fundamental band of physisorbed H_2. Distinct vibrational, rotational, and adsorbate phonon features induced by surface and intermolecular interactions are identified. When compared with adsorption isotherms, the surface-enhanced vibrational line saturates at 40% of the surface-layer coverage; this results from the short range of the surface-induced dipole in Steele's bilayer model and is inconsistent with a high-density monolayer phase. Our results also strongly point to the formation of islands at low coverages.

PACS numbers: 68.45.−v, 67.70.+n, 68.90.+g, 78.30.−j

Recently there has been considerable interest in the physics of adsorbates on porous substrates. When adsorption on these materials is modeled, it is assumed that adsorbate molecules overlay the surface at the pressure corresponding to the first step of the adsorption isotherm. However, estimates based on the Brunauer-Emmett-Teller (BET) model for the surface densities of helium, hydrogen, and to a lesser extent neon, result in anomalously large values.[1] Although this phenomenon has been known for more than thirty years and the state of the adsorbed layer is relevant to a variety of low-temperature experiments,[2,3] a microscopic understanding of the underlying physics has been lacking. With helium and hydrogen being very compressible, it is conceivable that the nearest-neighbor distance could be considerably reduced from that of the material inside the pores as a result of surface forces. However, calculations[4] suggest that the zero-point energy is large enough to compensate for the van der Waals forces. In order to explain the adsorption isotherms, a phenomenological model has been proposed in which two layers are coadsorbed at low saturations.[5] Here we report on experiments of infrared absorption of H_2 adsorbed on porous Vycor glass which directly test the bilayer model with rather remarkable results. Two spectroscopic techniques, neutron inelastic scattering[6] and electron-energy-loss spectroscopy[7] have been previously applied with success to the study of the rotational state and excitation spectrum of adsorbed H_2. For these methods, however, the physical processes that give rise to scattering are those already present in the isolated molecule. In contrast, infrared absorption of the fundamental band of H_2 is known to arise from overlap and intermolecular interactions in the bulk,[8] dissolved H_2,[9] and H_2–rare-gas complexes.[10] We will show that for adsorbed H_2 infrared-absorption spectroscopy provides a unique probe of the density profile across the surface. The surface-enhanced vibrational line and its side band from adsorbate phonons are presented for the first time and are explained, with use of the bulk H_2 results as a guide, by taking into account the appropriate surface parameters. The large enhancement (by a factor of 60), from the bulk (liquid) H_2 line intensity which is observed, is directly attributable to the larger induced dipole moment per molecule at the surface as compared with that induced by the weaker intermolecular interactions. Nevertheless, the vibrational effective charge of H_2 on Vycor is still 1 to 2 orders of magnitude smaller than that of the permanent-dipole adsorbates usually investigated[11]; thus is the relevance of a large–surface-to-volume–ratio substrate for the observation of the phenomena presented here. Although substantially broadened by the anisotropic part of the surface interactions, the intensity per molecule of the rotational-vibrational line at submonolayer coverages is not otherwise changed from that in the bulk and suggests the formation of islands of H_2 in porous Vycor glass at low temperatures. A model of islands based on the heterogeneity of the adsorption potential has been proposed for ^{4}He in Vycor by Roy and Halsey[12] in order to explain a dominant Fermi term in the specific heat at low temperatures.

The Vycor sample (Corning 7930) was a disk 3.58 mm in diameter and 3.5 mm thick. It was prepared by mechanical polishing, boiling in solutions of 30% H_2O_2, rinsing in boiling deionized water, and drying at 150 °C in a vacuum for 2 h. The sample was contained in a closely fitting copper cell with sapphire windows which was connected to a gas-handling system through a capillary tube and mounted in a closed-cycle refrigerator capable of reaching 10 K. Cell temperatures were measured with a calibrated germanium resistance thermometer. Standard volumetric techniques were used to measure the amount of nitrogen adsorbed by the sample at 77 K. A BET fit to the low-coverage data defines the N_2 monolayer coverage. With the assumption of cylindrical channels and an area density of 0.0617 $\mathrm{Å}^{-2}$, a 35-Å pore radius is obtained. We also measured adsorption isotherms of H_2 at 18 K using Vycor samples in which the infrared absorption was investigated. From a fit of the low-coverage data by the BET equation, we obtain a surface-layer coverage $n_0 = 3.5\times10^{-3}$ mol/cm^3, corresponding to a density $n_s=0.12$ Å^{-2}.

Infrared-absorption spectra were measured with a single-beam dispersive spectrometer based on a 0.25-m monochromator (5-cm^{-1} resolution) and a PbS detector. Figure 1 shows the absorbance $A=\log_{10}(I_0/I)$ measured for two adsorption stages at 18 K. The 80-K spectrum is also shown. The reference intensity I_0 is that which is transmitted through the bare Vycor at the same temperature. The H_2 adsorption isotherm at 18 K, measured with the infrared beam on, is presented in the inset. The large absorption peak at 4124 cm^{-1} in curve *b* is the surface vibrational line Q_1 corresponding to a transition from the intramolecular H_2 vibrational fundamental to the first excited state. Its FWHM is 22 cm^{-1}. When compared with the vibrational transition in the Raman spectra of the low-density gas phase a shift of 31 cm^{-1} towards the low-energy side is observed. The frequency shift is mainly a measure of the molecular distortion by the surface.[13] From the measurements done on samples with varying orthohydrogen-parahydrogen ratio we determine these shifts to be independent of the angular distribution of the molecules. For bulk H_2, the main contribution to vibrational shifts arises from the anharmonicity of the intramolecular potential.[14] With the extension of the theoretical models developed for the vibrational state of the bulk to adsorbed H_2, the frequency shift is

$$\delta\omega_e/\omega_e=1.5\lambda^2 a_1 F_s, \qquad (1)$$

where $\lambda=0.1663$ and $a_1=-1.607$ are anharmonicity constants of the hydrogen molecule. $F_s=-(r_e/\omega_e)V_s'$ is the potential-strength parameter, with V_s the potential-energy eigenvalue; the prime indicates derivatives with respect to r evaluated at $r_e=0.74$ Å, the equilibrium intramolecular distance. From (1) and the frequency shift we obtain $F_s=0.11$. For comparison, the corresponding parameter for solid (or liquid) H_2 is 0.04. We also obtain $(r_{es}-r_e)/r_e=8\times10^{-3}$, where r_{es} is the physisorbed H_2 intramolecular distance, corresponding to a very small modification of the molecule. To our knowledge, H_2 vibrational shifts have not been previously evaluated for the case of a surface. Such calculations involve a tradeoff between a red shift from the attractive part of the potential and a blue shift from the short-range repulsion. We have chosen the simple phenomenological surface potential given by Hoinkes,[15] which allows treating the two parts self-consistently. The potential minimum is $V_s=-C/r_g^3$, where r_g is the Lennard-Jones radius. With C proportional to the molecule polarizability, we get $V_s'=V_s(\alpha'/\alpha-3r_g'/r_g)$, where $\alpha'=1.07$ Å^2 and $\alpha=0.80$ Å^3.[16,17] The second term results from the short-range repulsion. An estimate for r_g' can be obtained from the following argument: r_g of the isolated molecule is 1.43 Å and corresponds to $r=r_e$. For a molecule with zero intramolecular separation r_g is that of the ^{4}He atom ($r_g=1.31$ Å).[18] Therefore, $r_g'/r_g=0.11$ Å^{-1}. We thus obtain $V_s=620$ cm^{-1}. This value is not inconsistent with a typical adsorption potential of H_2 on surfaces (300 cm^{-1}), with consideration of the approximations involved in the calculation. Surface potential heterogeneity can account for the FWHM and the small shift (5 cm^{-1}) with coverage. We point out that we have assumed that the dependence of V_s on the vibrational states can be ignored.

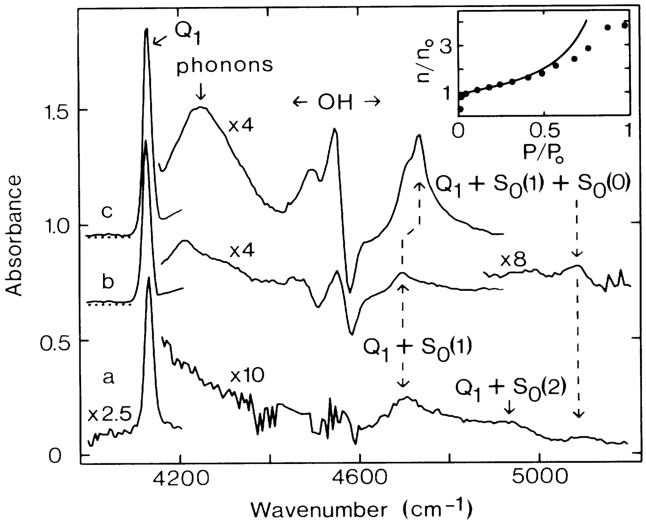

FIG. 1. Infrared-absorption spectra of normal H_2 on porous Vycor glass. Curve *a* corresponds to $T=80$ K at 3 atm pressure. Curves *b* and *c*, taken at 18 K, correspond to $n_s=0.6n_0$ and full pores, respectively. These curves have been displaced vertically by arbitrary amounts for clarity; the dotted line represents the base line in each case. Inset: Adsorption isotherm of H_2 on porous Vycor glass ($T=18$ K). Representative experimental data points are shown as filled circles. P_0 is the bulk condensation pressure. The BET-fit (solid line) surface-layer coverage n_0 is 3.5×10^{-3} mol cm^{-3}.

As shown in Fig. 2(a), the integrated absorptions of the Q_1 line and of its high-energy side band (labeled phonons in Fig. 1) saturate at coverages close to 1.8×10^{-3} mol cm^{-3}. Comparison with the adsorption isotherms reveals that saturation occurs at about half the surface-layer coverage defined by a BET fit to the adsorption data. The bilayer model could account for our observations when we consider the short range of the surface-induced dipole. A van der Waals–induced dipole shows a z^{-4} dependence,[19] with z the distance to the reference plane, resulting in a z^{-8} dependence of the infrared absorption. An even stronger z dependence is expected for dipoles induced by short-range interactions.[10] The strength of the induced dipole decaying away from the surface faster than that of the adsorption potential would result in a small contribution from the second layer to the measured infrared absorption.

The broad high-energy side band of the vibrational transition results from the combined excitation of the H_2 vibrational and a low-frequency mode. For full pores (curve *c* of Fig. 1), the band shape is similar to that exhibited by liquid H_2 and is interpreted as resulting from

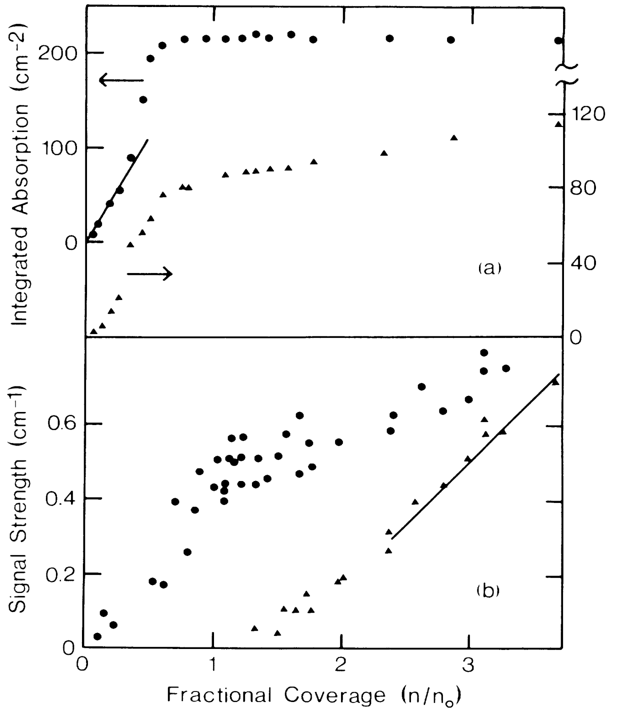

FIG. 2. (a) Coverage dependence of the Q_1-vibrational-line integrated absorption (filled circles) and of its side band (filled triangles). The solid line corresponds to an effective charge $e^* = 0.0061e$/molecule. (b) Signal strength (absorbance per unit length) of the surface (filled circles) and bulk (filled triangles) rotational-vibrational line $Q_1+S_0(1)$. The solid-line slope is 109 cm^2 mol^{-1}; the corresponding value for liquid H_2 is 72 cm^2 mol^{-1}.

phonon emission. The band maximum is shifted from the value corresponding to bulk H_2 (4223 cm^{-1}) to 4250 cm^{-1}. Estimates of the actual position of the phonon density-of-states maximum for full pores are model dependent as contributions from molecules with shifted vibrational frequencies (surface H_2), unshifted frequencies (H_2 in the pores), and two different excitation mechanisms (intermolecular and surface) are present. The low-coverage signal (curve *b* of Fig. 1) shows a Q_1 side band at 4218 cm^{-1}, suggesting the activation of a low-frequency mode of 94 cm^{-1} by the vibrational transition. For comparison, the absorption spectra of H_2 dissolved in silica[9] show a one-phonon line with a maximum at 4395 cm^{-1} corresponding to the lowest characteristic frequency of localized modes in the silica network ($\nu_2 = 250$ cm^{-1}). The absence of structure at that frequency in our spectra is an indication that H_2 inside the pores is not coupled to such modes. Instead, the observed side band is interpreted as vibrational coupling to the adsorbate phonons. Abrupt spectral changes of the phonon replica are observed as the temperature is increased above 40 K. This is believed to reflect a solid-gas phase transition, similar to that observed in amorphous silicon at 30 K,[20] with the spectral changes resulting from a sharp drop of the high-energy density of states at the transition. A comparison with the spectra obtained by neutron inelastic scattering for H_2 on Grafoil[6] is most revealing. In that case, a line measured for coverages below 1 monolayer is identified as involving a localized mode at 40 cm^{-1}. For coverages above 1 monolayer, the line broadens and is then identified as phononlike. No such changes with coverage are observed in our spectra, consistent with the formation of islands and the bilayer model which preclude large density changes in the film, and contrasting with the high-density monolayer model which is thought to apply to H_2 on Grafoil.

The peak at 4735 cm^{-1} in Fig. 1(c) appears for multilayer coverages. Its frequency agrees with that of the strong double transition $Q_1+S_0(J=1)$ (i.e., the two-molecule vibrational-rotational transition induced by quadrupole interactions) within the experimental resolution. Its intensity dependence on coverage is shown in Fig. 2(b). The signal strength per molecule exhibited by this feature corresponds to that found in liquid H_2 within 30%. Note that its intensity rises at surface-layer coverages and thus provides evidence, independently of the adsorption isotherm, for the surface-potential range. For submonolayer coverages, a peak is observed at 4695 cm^{-1} (curve *b* of Fig. 1) and its intensity as a function coverage is also shown in Fig. 2(b). The slope is roughly that of the bulk $Q_1+S_0(1)$ line, which indicate a common origin. The 40-cm^{-1} shift can be accounted for by consideration of the shift of the vibrational line (31 cm^{-1}) and a 1-cm^{-1} decrease of the rotational constant B_e resulting from the change in the average intramolecular distance (frequency shift of $10B_e$). Although the modification of the rotational state is small, judging from the frequency shifts, a width of approximately 50 cm^{-1} is observed. This can be understood in terms of the anisotropic part of the H_2-surface interaction which splits both initial and final states; the observed linewidth results from a number of unresolved transitions. This effect and the calculation of the intensities of the vibrational-rotational transitions will be discussed elsewhere.[21] The identification of the two-molecule process at submonolayer coverages strongly suggests the formation of islands in adsorbed H_2. Further indication is the observation of the surface $Q_1+S_0(0)+S_0(1)$ line at 5090 cm^{-1}, which involves the pairing of orthohydrogen and parahydrogen molecules. Also, specific-heat measurements of p-H_2 on Vycor have been recently interpreted in terms of an islands model.[22]

The band labeled OH in Fig. 1 arises from a shift upon H_2 adsorption of a broad hydroxyl absorption present in bare Vycor. The dispersive shape results from the effect of the frequency shift on the absorbance. This effect is well known and has been observed for other adsorbates, such as N_2.[23] The strength of this band rises steadily with coverage and shows no indication of preferential adsorption by the hydroxyl.

The phonon spectra are clearly inconsistent with a high-density monolayer phase for H_2 on Vycor. We have further considered the possibility that the surface-induced dipole saturation results from depolarization effects.[24] This would occur for $10\alpha n_s^{3/2} \simeq 1$. The value of α required for depolarization to become effective at 40% coverage, about ten times that of the gas phase, is considered unrealistic, particularly in view of the good agreement obtained with Eq. (1). Such a large modification of α would also change the rotational intensities drastically, which we have not observed.

In summary, the use of a porous substrate has enabled us to observe the characteristic spectrum of physisorbed H_2. We have shown that this unique approach provides novel information and insights into the state of simple adsorbates. This work not only can be extended to other transparent porous solids and, in general, to dispersed hydrogen, but also provides a basis for the attempting of experiments with well-characterized surfaces. Such experiments might help clarify the role of the substrate geometry in the bilayer structure.

The authors wish to thank L. Blum, J. M. Drake, H. J. Maris, and G. M. Seidel for helpful discussions. This work was partially supported by the National Science Foundation (Experimental Program to Stimulate Competitive Research).

---

[1] W. A. Steele and G. D. Halsey, Jr., J. Phys. Chem. **59**, 57 (1955).

[2] Cao Lie-zhao, D. F. Brewer, C. Girit, E. N. Smith, and J. D. Reppy, Phys. Rev. B **33**, 106 (1986).

[3] J. L. Tell and H. J. Maris, Phys. Rev. B **28**, 5122 (1983).

[4] H. Matsuda and C. J. N. Van den Meijdenberg, Physica (Utrecht) **26**, 939 (1960).

[5] W. A. Steele, J. Chem. Phys. **25**, 819 (1956).

[6] M. Nielsen and W. Ellensen, in *Proceedings of the Fourteenth International Conference on Low Temperature Physics, Otaniemi, Finland, 1975,* edited by M. Krusius and M. Vuorio (North-Holland, Amsterdam, 1975), Vol. 4, p. 437; I. F. Silvera and M. Nielsen, Phys. Rev. Lett. **37**, 1275 (1976).

[7] Ph. Avouris, D. Schmeisser, and J. E. Demuth, Phys. Rev. Lett. **48**, 199 (1982).

[8] H. P. Gush, W. F. G. Hare, E. J. Allin, and H. L. Welsh, Can. J. Phys. **38**, 176 (1960).

[9] H. L. Welsh and R. T. Kriegler, J. Chem. Phys. **50**, 1043 (1969), and references therein; C. M. Hartwig and J. Vitko, Jr., Phys. Rev. B **18**, 3006 (1978).

[10] For a review, see J. Van Kranendonk, Physica (Utrecht) **73**, 156 (1974).

[11] H. Ibach, Surf. Sci. **66**, 56 (1977).

[12] N. N. Roy and G. D. Halsey, J. Low Temp. Phys. **4**, 231 (1971).

[13] The density of 1 monolayer, 0.12 $Å^{-2}$, corresponds to a bulk hydrostatic pressure of 10 kbar. This would result in a frequency shift of only 8 cm^{-1} towards high energies. See, S. K. Sharma, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **44**, 886 (1980).

[14] J. Van Kranendonk and G. Karl, Rev. Mod. Phys. **40**, 531 (1968).

[15] H. Hoinkes, Rev. Mod. Phys. **52**, 933 (1980).

[16] M. F. Crawford and R. E. MacDonald, Can. J. Phys. **6**, 1022 (1958).

[17] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[18] J. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), Table I-A.

[19] For a discussion, see R. A. Kromhout and B. Linder, J. Chem. Phys. **81**, 2516 (1984).

[20] Y. J. Chabal and C. K. N. Patel, Phys. Rev. Lett. **53**, 1771 (1984).

[21] T. E. Huber and C. A. Huber, to be published.

[22] H. J. Maris, private communication.

[23] R. S. MacDonald, J. Am. Chem. Soc. **70**, 850 (1957).

[24] P. Hollins and J. Pritchard, *Vibrational Spectroscopy of Adsorbates,* edited by R. F. Willis (Springer-Verlag, New York, 1980).