PHYSICAL REVIEW B VOLUME 40, NUMBER 18 15 DECEMBER 1989-II

# Vibrational overtone absorption of interfacial hydrogen in porous Vycor glass

T. E. Huber* and C. A. Huber†
*Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931*

(Received 25 April 1989)

The first measurements of the overtone absorption spectrum of $H_2$ and $D_2$ in samples of porous Vycor glass are reported. The single-molecule vibrational overtone and the combination of the intramolecular vibrational fundamental with the surface hydroxyl fundamental are observed. The measured frequencies can be explained, with use of the results for bulk $H_2$ as a guide, by taking into account appropriate surface parameters. It is also found that the overtone absorption of interfacial $H_2$ is enhanced by a factor of 150 from that of the bulk liquid. The observation of these otherwise weak spectral features provides important data for the extension of vibrational spectroscopic treatments to molecular hydrogen on surfaces, particularly in regard to induced dipole moments, electrical and mechanical anharmonicities, and dissociation energies.

Recent interest[1,2] in the structure of adsorbed $H_2$ in porous materials has motivated this experimental work on the applicability of the infrared-absorption technique to the study of physisorbed $H_2$. Infrared absorption of the fundamental band of $H_2$ in the bulk[3] and in $H_2$–rare-gas complexes[4] is known to arise from overlap and quadrupolar interactions. For adsorbed $H_2$, in addition to intermolecular interactions, an interfacial mechanism of inducing absorption has been identified in porous Vycor glass. A large enhancement of the fundamental vibrational line (by a factor of 60) from the bulk $H_2$ line intensity has been observed.[5] The enhancement is directly attributable to the larger induced dipole moment per molecule at the surface as compared with that induced by the weaker intermolecular interactions. Infrared absorption at the vibrational frequencies results from the dependence of the surface interactions on the vibrational coordinate. Although there is some disagreement as to the specific surface interaction that originates the surface-induced dipole in adsorbate films, proposals range from van der Waals interactions to surface electrical[6] charges, the phenomenon is generally expected for any surface. There are reasons to believe that a van der Waals surface-induced dipole appears self-consistently with van der Waals surface forces. Porous Vycor glass (PVG) is a popular substrate for low-temperature physisorption studies of light adsorbates[1] and the understanding of the interfacial state of matter in Vycor is important. In a previous study of $H_2$ in PVG we have observed vibrational and ro-vibrational lines: the former are surface induced, the latter are induced by intermolecular interactions.[5] As a whole the vibrational and rotational eigenmodes of the molecule are only slightly modified by the surface. For instance, the molecule rotates freely on the surface and the vibrational frequency $Q_1$ at 4124 $\text{cm}^{-1}$, is red shifted by only 31 $\text{cm}^{-1}$ from the frequency of the isolated molecule, such shifts being explained from a physical adsorption model. Vycor has also been used as a prototype absorbant for photodesorption studies. A better understanding of the optical absorption of interfacial $H_2$ would help settle some longstanding arguments in this field.[7]

Our results indicate that large surface-area-to-volume materials might still be needed to investigate optical phenomena involving physisorbed $H_2$. The vibrational effective charge $H_2$ on Vycor is 1–2 orders of magnitude smaller than that of the permanent dipole adsorbates usually investigated in infrared-absorption surface spectroscopy. Detailed PVG surface models are available[8] which show that the material is very heterogeneous. In order to understand if impurities in PVG, such as boron, might be involved in the surface-induced absorption we have also studied the fundamental vibrational of $H_2$ and $D_2$ in porous silica gel and in Mgo sintered pills.[9,10] From our experiments the conclusion in this regard is that the infrared absorption is induced on surfaces by a rather general mechanism and is not necessarily tied to the presence of impurities. Clearly, more work is needed to understand the optical absorption of $H_2$ on surfaces. In this context, overtone spectra are important to develop molecular vibrational models of physisorbed species. Overtone spectra of fundamental intramolecular vibrational modes in the gaseous and condensed phases of complex molecules such as benzene[11] have been extensively studied. In such cases the overtone absorption results from the single-molecule properties and condensed-matter effects are seen only as modifications of band positions and widths. In contrast, the homonuclear $H_2$ and $D_2$ show a very weak overtone spectrum at low pressures. McKellar and Welsh[12] have summarized the high-pressure-gas data for the second harmonic of $H_2$ and have shown that in the region of 30–40 amagat and at a temperature of 80 K a description based on binary collisions reasonably explains the observed intensities. In solid $H_2$ the weak absorptions at the second and third harmonics of the fundamental vibration have been studied using optoacoustic spectroscopic methods. In that case only combination bands, that is, bimolecular features, were observed in the overtone region.[13] We have measured the first overtone spectra of $H_2$ and $D_2$ adsorbed on porous Vycor glass and of liquid $H_2$. These spectra indicate that both single- and two-particle absorption lines arise in the liquid from quadrupole induction. On the other hand, the spectrum of surface $H_2$ is characteristically interfacial and not intermolecular, in the sense that the highest intensity features involve a single hydrogen molecule. The same conclusion has to be drawn from the dependence of the infrared absorption on coverage for $H_2$ and $D_2$. Measurements of the absorption spectrum of mixtures of $H_2$ and $D_2$ were also carried out searching for evidence of intermolecular coupling with negative results. Such results are also discussed here. It is also found that the integrated absorption per molecule of the overtone of $H_2$ on Vycor is enhanced from that of bulk liquid by a factor close to 150. This result is given for reference purposes. In contrast to the case of bulk $H_2$ where bimolecular processes are relevant and in similarity to the fundamental absorption spectrum of adsorbed $H_2$, the dipole moment induced by the surface is the dominant mechanism leading to the infrared absorption in the overtone region. Based on this identification, a calculation for the ratio of the absorption at the overtone frequency to that at the fundamental is presented which indicates that electrical anharmonicities plays an important role for adsorbed $H_2$. Also, the dissociation energy of adsorbed $H_2$ can be estimated from the data to be increased by only 0.7%. The absorption spectra presented here remind one of those of silica fibers,[14] which have been studied extensively for vibrational overtone absorptions. However, in the surface phase of $H_2$, in addition to the pure overtone absorption which singly dominates the overtone region for $H_2$ in an optical fiber, a combination of the intramolecular vibrational fundamental with the Si—OH stretch is also observed. The absorbent used in this study was a rod-shaped piece of porous Vycor glass (Corning code 7930) 3.6 mm in diameter and 2.9 mm thick. From a fit of low-coverage data of the $N_2$ adsorption isotherm to the Brunaver, Emmett, and Teller[10] (BET) equation we obtain an area of 205 $m^2/cm^3$ of sample and a 30-Å pore radius. The sample was contained in a closely fitting copper cell with sapphire windows which was connected to a gas-handling system. Infrared-absorption spectra were measured with a single beam dispersive spectrophotometer based on a 0.25-m monochromator and a PbS thermoelectrically cooled detector. The system achieved a 10-$cm^{-1}$ wave-number resolution in the region of the overtone spectrum of $H_2$. Figure 1 shows the absorbance $A = \log_{10}(I_0/I)$ measured for adsorbed $H_2$ and $D_2$. $I$ in the transmission of Vycor with the adsorbate, the reference intensity $I_0$ is that which is transmitted through the bare Vycor at the same temperature. Curve *a* of Fig. 1 corresponds to a coverage $n_s = 2.9$ $mmol/cm^3$ of $H_2$ at 18 K. A BET fit to the adsorption isotherm of $H_2$ on a sample of porous Vycor glass from the same batch as the one used for the optical measurements gives a surface-layer coverage $n_0$ of 3.5 $mmol/cm^3$. Therefore the fractional coverage of $H_2$ at which the spectrum shown in curve *a* was taken is $n_s = 0.83 n_0$.

The strongest feature found in the overtone region is the band labeled OH in Fig. 1. It arises from the frequency shift upon $H_2$ (or $D_2$) adsorption of the broad hydroxyl absorption present in bare Vycor. The frequency shifts of the hydroxyls at the surface upon adsorption of hydrogen are studied elsewhere.[10] The sharp peak at 8150 $cm^{-1}$ is an artifact also and originates from the shift of a prominent step at that frequency.

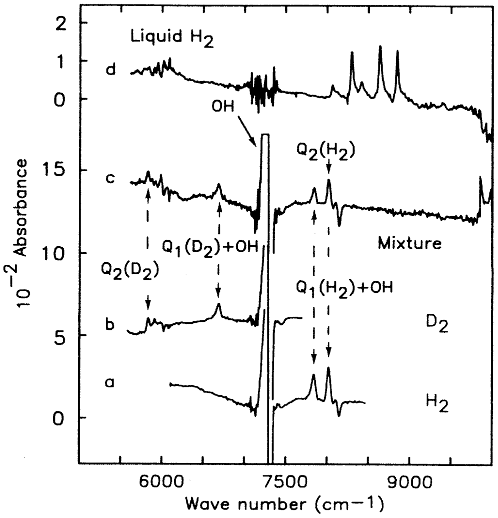

FIG. 1. Infrared-absorption spectra of hydrogen in porous Vycor glass in the vibrational overtone region. Curve *a* corresponds to $H_2$ at 18 K and a coverage $n_s = 2.9$ $mmol/cm^3$. Curve *b* corresponds to $D_2$ at 20 K and $n_s = 2.8$ $mmol/cm^3$. Curve *c* corresponds to a mixture of $H_2$ and $D_2$ as explained in the text. Curve *d* is the absorption spectrum of liquid $H_2$ at 18 K. The curves have been displaced vertically by arbitrary amounts for clarity. The BET surface layer coverage of $H_2$, $n_0$, is 3.5 $mmol/cm^3$ at 18 K.

The strong absorption peak in the spectrum of adsorbed $H_2$ at 8020 $cm^{-1}$ in curve *a* of Fig. 1 is very close to the transition frequency of the single-particle overtone $Q_2$ and is identified as such. The $Q_2$ transition can be estimated to be at 8087 $cm^{-1}$ for an anharmonic isolated molecule.[15] The gas at low temperatures absorbs radiation at roughly 8000 $cm^{-1}$, the full width at half maximum (FWHM) of the absorption line being over 100 $cm^{-1}$. In contrast, the $Q_2$ feature for adsorbed $H_2$ has a FWHM of only 35 $cm^{-1}$. Furthermore, a 67-$cm^{-1}$ red shift is observed from the isolated-molecule frequency of the overtone $Q_2$. The frequency shift is a measure of the molecular distortion at the surface. Neglecting rotational effects on the vibrational transition energy levels, the shift of the overtone vibrational frequency $\nu(Q_2)$ is

$$\delta\nu(Q_2) = 2\delta\nu(Q_1) - 2\delta(\omega_e x_e) \qquad (1)$$

where $\omega_e x_e$ is the anharmonicity parameter and $\nu(Q_1)$ is the fundamental vibrational frequency. From the measured frequency shifts we obtain that the anharmonicity parameter is decreased by only 2.5 $cm^{-1}$ by the presence of the surface from the 121-$cm^{-1}$ value calculated for an isolated molecule.[15] This result is not unexpected for weakly adsorbed molecules.[16] The broader absorption peak at 7820 $cm^{-1}$ in curve *a* is believed to be a hydroxyl-$H_2$ combination absorption band. It involves the simultaneous excitation of the surface hydroxyl and of a $H_2$ molecule. In the absence of vibrational coupling, the frequency of the combination band can be calculated from the $Q_1$ transition frequency (4124 $cm^{-1}$ for $H_2$ on Vycor) and the OH transition frequency (3750 $cm^{-1}$). The 7874-$cm^{-1}$ value obtained from this simple estimate should be contrasted with the 7905 $cm^{-1}$ calculated for the isolated molecule (Table I). Although not inconsistent with the measured value of 7820 $cm^{-1}$, a better estimate for the combination frequency should incorporate condensed state effects, such as the coupling between vibrational motion of neighboring hydroxyls and adsorbed molecules. Such effects have been considered for neighboring molecules in solid $H_2$.[15] The vibrational frequencies of interfacial $H_2$ in the overtone region are summarized in Table I, together with assignments of the absorption lines and their corresponding frequencies calculated from the parameters of the isolated $H_2$ molecule. We have also measured the infrared absorption of deuterium in porous Vycor glass. The overtone spectrum of $D_2$ on Vycor is shown in curve *b* of Fig. 1. Quantitative information about the $D_2$ spectrum is presented in Table I. The $Q_1$ frequency of $D_2$ on Vycor has not been measured directly. Instead, we use the value obtained for $D_2$ on silica gels[9] which is 2967 $cm^{-1}$ (this is believed to be a good approximation within our frequency resolution). In the absence of vibrational coupling, the frequency of the combination band can be calculated from the $Q_1$ frequency and the OH transition frequency. We obtain a value of 6717 $cm^{-1}$. The experimental value is 6690 $cm^{-1}$. The experimental value obtained for the $Q_2$ frequency of $D_2$ is 5820 $cm^{-1}$. The $D_2$ data is compared to the vibrational frequencies of the isolated molecule calculated in Ref. 17.

As shown in Fig. 2, the signal strength of the prominent lines, that is, the $Q_2$ and $Q_1$+OH lines of adsorbed $H_2$ and $D_2$ saturate at near monolayer coverages. This indicates that the overtone vibrational absorption is activated by the surface and that this mechanism is short ranged. In order to further show that the origin of the infrared absorption in interfacial $H_2$ is different from that in the bulk it is important to compare absolute absorption strengths for $H_2$ in the two environments. The FWHM of the $Q_2$ line in the liquid is 30 $cm^{-1}$, the resulting integrated absorption is 6.4 cm/mol. For adsorbed $H_2$ at a coverage of 2 $mmol/cm^3$ we obtain an absorption of 960 cm/mol. Thus the overtone absorption in adsorbed $H_2$ is enhanced by a factor of 150 from that of the liquid bulk, the enhancement arising from the stronger surface interactions in comparison with intermolecular interactions. This enhancement factor is given here mostly for reference purposes, i.e., since the infrared absorption in the bulk phases is a two-molecule process, special selection rules and condensed state effects have to be taken into account when calculating the absorption in liquid $H_2$. This type of calculation is beyond the scope of this work.

TABLE I. First overtone absorption spectrum of liquid and adsorbed hydrogen. Absorbances of the absorption lines of adsorbed $H_2$ and $D_2$ correspond to coverages for which the signal saturates. Combination band frequencies have been calculated by adding the frequencies of transitions involved. When the transition frequency is $J$ dependent the $J=0$ result has been used.

| Observed frequency ($cm^{-1}$) | Absorbance ($10^2$) | Identification | Calculated frequency ($cm^{-1}$) |
|---|---|---|---|
| | | I. Liquid hydrogen | |
| 8070 | 0.38 | $Q_2$ | 8087[a] |
| 8305 | 1.2 | $Q_1+Q_1$ | 8310 |
| 8420 | 0.45 | $Q_2+S_0(0)$ | 8441 |
| 8640 | 1.5 | $Q_2+S_0(1)$ | 8674 |
| 8855 | 1.4 | $Q_1+S_1(1)$ | 8867 |
| | | II. Adsorbed $H_2$ | |
| 7820 | 2.2 | $Q_1$+OH | 7905 |
| 8020 | 2.4 | $Q_2$ | 8087 |
| | | III. Adsorbed $D_2$ | |
| 5820 | 0.9 | $Q_2$ | 5850[b] |
| 6690 | 1.1 | $Q_1$+OH | 6740 |

[a] Reference 16.

[b] Reference 17.

The absence of a feature identifiable as $Q_1+Q_1$ is an indication that the surface mechanism is dominant. Furthermore, it is well known that the first overtone spectrum of bulk $H_2$ results from quadrupole induction between hydrogen molecules.[12,13] The role of overlap interactions in the induction of molecular dipole moments has been previously tested[3] by varying the ortho-$H_2$ to para-$H_2$ ratio. A similar study was undertaken here. Contrary to the case of condensed $H_2$, we have not observed any changes in frequencies or intensities which could be traced to the varying ortho-$H_2$ to para-$H_2$ ratio. Rather, the overtone enhancement we observe is simply linked, as the enhancement of the vibrational fundamental, to a surface-induced dipole. The dipole induced on molecules on the surface can be treated in analogy to the permanent dipole that molecules, such as CO, retain from the bulk phase when adsorbed. For this case Herman and Shuler[18] derived an expression for the ratio of the absorption at the overtone frequency $A^{2,0}$ to that of the fundamental $A^{1,0}$. Neglecting electrical anharmonicity one obtains $A^{2,0}/A^{1,0}=8/15x_e=0.015$ for $H^2$. From the data in Table I and in Ref. 5 the experimental ratio is 0.028. This result suggests that electrical anharmonicity plays an important role for adsorbed $H_2$.

In order to test the assignments of the absorption lines observed for $H_2$ and $D_2$ on Vycor we have studied the ab-

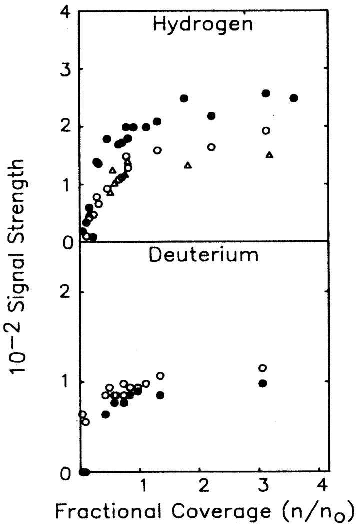

FIG. 2. Coverage dependence of the overtone features signal strength showing that enhancement of the infrared absorption is interfacial in origin. Open circles correspond to OH+$Q_1$ lines. Solid circles correspond to $Q_2$ lines. Open triangles indicate the OH+$Q_1$ line of para-$H_2$. The Vycor pores are full of hydrogen for $n=3.8n_0$. The lines' signal strengths can be determined within about ±0.1 for $H_2$ and ±0.15 for $D_2$.

sorption spectra of mixtures of the isotopes adsorbed on the surface of Vycor. The spectrum of a mixture with $n_s = 3.2$ mmol/cm$^3$ and fractional $H_2$ concentration of 0.5 is shown in Fig. 1, curve *c*. Clearly, all the features in the absorption spectrum of the mixture are also present in one of the spectra of the pure phases. Furthermore, it can be shown that within the precision of the measurements the $Q_2$ and hydroxyl-$H_2$ (and-$D_2$) adsorption lines in the mixture have the same strength per molecule as they exhibit in the corresponding pure phase absorption spectrum. The absence of mixed-isotope combination lines, such as the $Q_1(H_2)+Q_1(D_2)$ combination, is consistent with our spectral identification. An intermolecular-induced dipole would result in strong combination lines in a mixture.[19] Such absence of mixed-isotope absorption could be interpreted in terms of an isotope-separated state of aggregation on the surface. However, the fact that hydrogen and deuterium mix well in the solid[20] and liquid[21] states argues strongly against that possibility.

It is known that $H_2$ diffused into silica optical fibers is infrared active,[14] the absorption spectrum of $H_2$ extending for the intramolecular fundamental vibration up to the third overtone region in the visible. In close similarity to the case of interfacial $H_2$, the strongest absorption feature is the $Q_1$ line followed by the overtone, $Q_2$, their intensity ratio being approximately the same as for interfacial $H_2$

In summary, we have studied the absorption spectra of $H_2$ and $D_2$ adsorbed in porous Vycor glass in the overtone region. To our knowledge this is the first time that the overtone absorption spectrum of molecular interfacial hydrogen on any surface has been recorded and analyzed. This observation only is made possible by the enhancement of the infrared absorption due to the surface-induced dipole and by the large specific area of PVG. The difference between the measured interfacial-$H_2$ (or -$D_2$) infrared-absorption frequencies and the values calculated for the isolated molecule can be understood in terms of surface interaction. Our data on interfacial hydrogen and those on dissolved hydrogen from other authors indicate the need to extend vibrational spectroscopic treatments of hydrogen in the condensed state to interstitial and surface sites. Based on the analogy shown here one can consider the system $H_2$-PVG, just as the system $H_2$ in glass, as a possible Raman-gain medium.[22] Our experimental work can be extended to other transparent solids and, in general, to dispersed $H_2$. It provides a basis for attempting infrared-absorption experiments on $H_2$ on better characterized surfaces.

The authors wish to thank L. Blum, H. J. Maris, and I. F. Silvera for helpful discussions. This work was supported by the National Science Foundation through its Experimental Program to Stimulate Competitive Research.

---

*Present address: Department of Physics, Harvard University, Cambridge, MA 02138.

†Present address: Francis Bitter National Magnet Laboratory, Massachussets Institute of Technology, Cambridge, MA 02139.

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

[2] J. Ma *et al.*, Phys. Rev. Lett. **61**, 2368 (1988).

[3] H. P. Gush *et al.*, Can. J. Phys. **38**, 176 (1960).

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

[5] T. E. Huber and C. A. Huber, Phys. Rev. Lett. **59**, 1120 (1987).

[6] B. Linder and R. A. Kromhout, J. Chem. Phys. **84**, 2753 (1986).

[7] T. J. Chuang, Surf. Sci. Rep. **3**, 1 (1983).

[8] M. L. Hair, *Infrared Spectroscopy in Surface Chemistry* (Dekker, New York, 1967).

[9] We present elsewhere measurements of the surface-enhanced infrared absorption of $H_2$ and $D_2$ adsorbed in a thin pellet of Davisil, a porous silica gel. The frequency shift of the $H_2$ vibrational fundamental is, within our frequency resolution of 5 cm$^{-1}$, the same as that of $H_2$ in PVG (Ref. 10). The vibrational frequency of adsorbed $D_2$, 2967 cm$^{-1}$, exhibits a red shift of 25 cm$^{-1}$. The integrated absorption of the $Q_1$ line per adsorbed $D_2$ molecule also compares favorably with the integrated absorption per molecule of $H_2$ on porous Vycor glass for low coverages. Preliminary measurements of the surface-induced absorption of $H_2$ on MgO sintered pills (Ref. 2) have also been done.

[10] T. E. Huber and C. A. Huber, J. Phys. Chem. (to be published).

[11] B. R. Henry, in *Vibrational Spectra and Structure*, edited by J. R. Durig (Elsevier, Amsterdam, 1981), Vol. 10.

[12] R. W. McKellar and H. L. Welsh, Proc. R. Soc. London, Ser. A **322**, 421 (1971); A. Watanabe, J. L. Hunt, and H. L. Welsh, Can. J. Phys. **49**, 861 (1971).

[13] C. K. N. Patel, E. T. Nelson, and R. J. Kerl, Phys. Rev. Lett. **47**, 1631 (1981).

[14] C. M. Hartwig and J. Vitko, Phys. Rev. B **18**, 3006 (1978); J. Stone *et al.*, Bell Syst. Tech. J. **63**, 991 (1984).

[15] B. P. Stoicheff, Can. J. Phys. **35**, 730 (1957); J. Van Kranendonk, Rev. Mod. Phys. **40**, 531 (1968).

[16] The anharmonicity parameter of $H_2$ is closely related to the dissociation energy $D$. If the potential energy curve is represented by a Morse potential the relation is $D=(\omega_e)^2/4(\omega_e x_e)$ where $\omega_e$ can be approximated by $\nu(Q_1)$. We then obtain that the overall change induced by the surface on the dissociation parameter $D$ is an increase of only 0.7%. For a calculation of the dissociation energy see G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nonstrand, Princeton, 1950).

[17] K. P. Huber, in *AIP Handbook*, 3rd ed., edited by D. E. Gray (McGraw-Hill, New York, 1972), Vol. 7, p. 168.

[18] R. C. Herman and K. E. Shuler, J. Chem. Phys. **22**, 481 (1954).

[19] The observation that the signal strength of the $Q_2(H_2)$ line in the spectrum of the mixture is proportional to the $H_2$ coverage, calculated as $n_s c$, where $c$ is the concentration, eliminates intermolecular interactions as a significant dipole-inducing mechanism for $H_2$ on Vycor. More sensitive tests were performed using low $H_2$ concentration mixtures with the same result.

[20] D. White and J. R. Gaines, J. Chem. Phys. **42**, 4150 (1965).

[21] N. G. Bereznyak *et al.*, Zh. Eksp. Teor. Fiz. **59**, 1534 (1970) [Sov. Phys.—JETP **32**, 838 (1971)].

[22] J. Stone, A. R. Chraplyvy, and C. A. Burrus, Opt. Lett. **7**, 297 (1982).