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Inelastic Neutron Scattering and Separation Coefficient of Absorbed Hydrogen: Molecular Alignment and Energy Levels

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Inelastic neutron scattering and measurement of the ortho-para separation coefficient have been used to study the low lying rotational states of molecular hydrogen adsorbed on activated alumina. The observations are consistent with a picture in which the orientational motion of the molecules is severely hindered. Results are analyzed in terms of two models: a two-dimensional rotor and an axially constrained rotor. The latter which is more consistent with the data serves to explain preferential adsorption of orthohydrogen.

In recent years there has been great activity in the study of the solid molecular hydrogens, especially in the orientationally ordered states of orthohydrogen (*o*-H₂) and paradeuterium (*p*-D₂).¹ These studies were made possible by our ability to prepare samples of these nonequilibrium metastable species in almost 100% pure concentrations by selective adsorption on activated alumina. Although this amazing technique has been developed and widely exploited for more than twenty years, a microscopic understanding of the underlying physics has lacked. Here, we study the energy levels and infer the orientational states of an adsorbed submonolayer of H₂ by means of inelastic neutron scattering. In addition we provide new measurements of the ortho-para separation coefficient *S* of H₂ and D₂ at 20.4 K to overcome interpretational difficulties with neutron data from which we can also determine *S*. We show that the large difference between our values of *S* and earlier ones arises at least in part from different crystal structures of samples identified as "activated alumina."

Sandler² first noted that at low temperatures, the ortho-para concentration ratio of hydrogen adsorbed on TiO₂ was greater than that of the gas reservoir from which it was adsorbed. Cunningham, Chapin, and Johnston³ used this preferential adsorption on γ -alumina at 20.4 K to produce *o*-H₂ and *p*-D₂ and the technique was further developed by Depatie and Mills.⁴ Sandler suggested that the mechanism of preferential adsorption might lie in the confinement of the adsorbed molecules to rotation in two dimensions (2-D rotor). White and Lassetre⁵ studied the rotationally hindered hydrogen molecule theoretically but were

unable to explain the experimental results with their model. Here we show that the rotational spectrum of adsorbed H₂ is greatly distorted from that of a free molecule and analyze the results in terms of two barrier models⁵: (1) an axially symmetric orientational barrier confining the molecules to rotation in two dimensions, and (2) an axially confining potential, which in the extreme case would restrict the molecule from rotating. Our measurements support the second model, which for contrast and convenience we shall refer to as the 1-D vibrator.

The rotational properties of molecular hydrogen in the gaseous, liquid, and low-pressure solid state can be described by the free-rotor model (3-D rotor). This property also holds for H₂ adsorbed to certain surfaces such as Grafoil.⁶ The wave functions of the 3-D rotor are the spherical harmonics⁷ $Y_{jm}(\theta, \varphi)$ with a corresponding energy $E = BJ(J+1)$ where *J* is the rotational quantum number and $B = 59.3 \text{ cm}^{-1}$ (7.35 meV) for H₂ and 29.9 cm^{-1} (3.70 meV) for D₂. In two dimensions the rotational energy spectrum is given by $E = Bm^2$ where $m = 0, \pm 1, \pm 2, \dots$.⁷ The orbital wave functions are symmetric under permutation of the nucleons for $|m|$ even and antisymmetric for $|m|$ odd. The interaction with the surface does not mix the nuclear spin states which are used to identify the ortho and para species. When confined to one dimension the molecules can only vibrate.

For preferential adsorption, the separation coefficient defined as

$$S = (\rho_o^a / \rho_e^a) / (\rho_o^g / \rho_e^g) \quad (1)$$

must be greater than 1, where ρ_o^a / ρ_e^a is the ratio

of adsorbed mole fraction of odd and even rotational states (o and e correspond to ortho and para, respectively, for H_2 and to para and ortho, respectively, for D_2) and ρ_o^g/ρ_e^g is the corresponding ratio in the gas phase. An expression for S can be derived if the energy spectrum is known. White and Lassette⁵ studied the energy levels of an adsorbed diatomic molecule for the lowest term in the Taylor series expansion of the surface-molecule potential $V(z, \eta) = V(z_0, 0) + \Phi\eta^2 + K(z - z_0)^2$ with z the distance from the surface and $\eta = \cos\theta$, where θ is the angle between the molecular axis and the z direction. For positive Φ the molecule favors lying in the plane, going over to the 2-D rotor for $\Phi \rightarrow \infty$. For negative Φ it is more convenient to expand about $\sin\theta$ and define a positive barrier Φ' . For this barrier the molecules preferentially orient perpendicular to the surface; in the limit $\Phi' \rightarrow \infty$ the molecules are confined to one dimension and can only vibrate in the z direction. In Fig. 1(a) we show their results for the low lying rotational states as a function of the barrier height. Since each state of the hin-

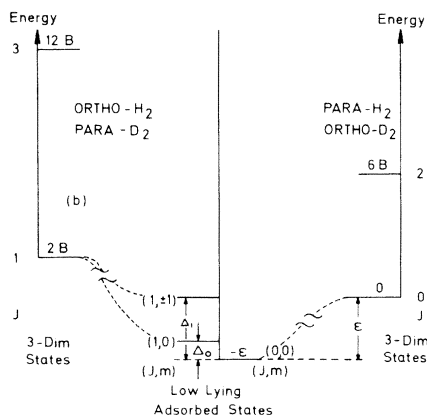
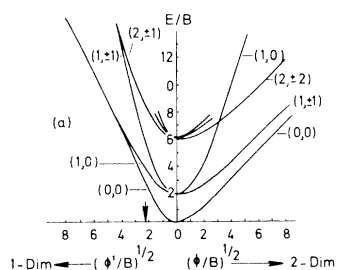


FIG. 1. (a) Energy E of the low-lying states of a hindered diatomic molecule as a function of the ratio of the barrier height, Φ , to the rotational constant B . (b) Low-lying energy levels of gas phase and adsorbed molecules for barrier height $\Phi' = 5B$ indicated by the arrow in (a).

dered rotor correlates with a state of the free rotor for $\Phi \rightarrow 0$, and J, m quantum numbers are used to identify the states. In Fig. 1(b) we show the energy levels of the free molecule and the adsorbed molecule at the barrier height indicated by the arrow in Fig. 1(a). For simplicity we assume that the adsorbed states are lowered in energy by an adsorption potential $\epsilon(\bar{r}_i)$ which can depend on site \bar{r}_i but is independent of the rotational states. Only the three lowest adsorbed states, $(J, m) = (0, 0)$, $(1, 0)$, and $(1, \pm 1)$, are considered because the splittings are large compared to experimental values of kT .

To calculate S , we assume that the surface-gas ortho species are in equilibrium with each other and likewise for the para species; no conversion is allowed in the gas or on the surface so that the ortho and para species are two independent systems. Then for H_2 , using Δ_0 and Δ_1 , shown in Fig. 1(b), we have

$$\rho_o^a/\rho_o^g = \{3 \exp[(\epsilon - \Delta_0)kT] + 6 \exp[(\epsilon - \Delta_1)kT]\} / 9e^{-2B/kT}, \quad (2a)$$

$$\rho_e^a/\rho_e^g = e^{\epsilon/kT}/1, \quad (2b)$$

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

where only the lowest rotational states are considered. Equation (3) is also applicable for D_2 . For the ideal 2-D rotor, $\Delta_1 = B$ and $\Delta_0 = \infty$ yielding $S = 43.8$ for H_2 and 5.45 for D_2 at 20.4 K. Measured or estimated values^{3, 8, 5} at 20.4 K on γ -alumina are 16 ± 3 for H_2 and 2.4 for D_2 , in poor agreement with the ideal 2-D rotor. For a completely hindered ideal 1-D vibrator $\Delta_0 = 0$ and $\Delta_1 = \infty$ yielding $S = 1439$ for H_2 and 22.3 for D_2 at 20.4 K.

In order to study the rotational states we have used the technique of inelastic neutron scattering. H_2 has a large spin incoherent neutron cross section and in this case a change in proton spin state means a para-ortho conversion transition. This transition has been observed in the solid⁹ and for H_2 adsorbed on Grafoil⁶ [see Figs. 2(a) and 2(b)]. In all of these cases the transition takes place at an energy $2B = 14.7$ meV as expected for a 3-D rotor. In the current experiment, samples of activated alumina (Alcoa Chemicals, grade F-1, mesh 8-14) consisting of small porous pebbles with linear dimensions of order 2-3 mm were heated to $\sim 120-140^\circ\text{C}$ to activate the surface. Samples were also pulverized and activated for an x-ray analysis of the composition. No indication of γ -alumina was found, but rather $\chi\text{-Al}_2\text{O}_3$

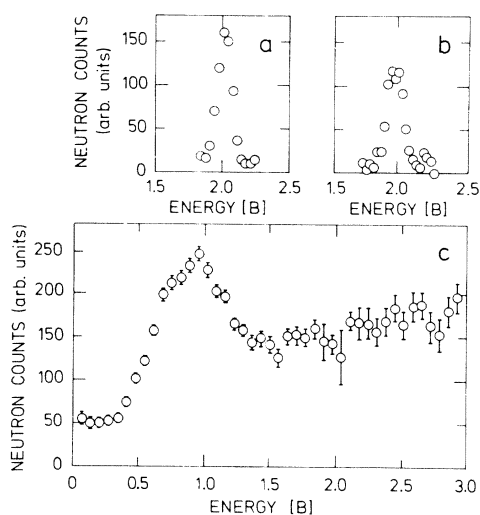


FIG. 2. Inelastic neutron scattering groups for (a) solid H₂, Ref. 9, (b) H₂ absorbed on Grafoil, Ref. 6, (c) H₂ absorbed on alumina. The amount of gas adsorbed per gram of alumina is 16.5 cm³ STP. Scattering counts from the bare alumina are subtracted off. The transferred momentum of the neutron is $\hbar Q$ where $Q = 2.25 \text{ \AA}^{-1}$; energy transfer is given in units of $B = 7.35 \text{ meV}$. Sample temperature was 5°K.

and γ -AlOOH were identified as the main constituents. Hydrogen which was first converted to 99% para species was adsorbed in various submonolayer coverages. Inelastic neutron-scattering groups were measured for a number of different scattering vectors and for sample temperatures from 5 to 77 K. The measurements were performed on a triple-axis spectrometer on the cold source beam of reactor DR3 at Risø. A representative spectrum is shown in Fig. 2(c). A broad peak centered at $\sim B$, the energy expected for a 2-D rotor, was observed, whereas no peak is seen at $2B$. At energies below $0.5B$ a weak scattering intensity is observed which may have arisen from multiple scattering; at energies

above $1.5B$ a broad, unstructured spectrum was obtained.

These data are very suggestive that adsorbed H₂ behaves as a 2-D rotor with the peak value of $\Delta_1 < B$ possibly arising from a strong interaction with the surface that affects the molecular electronic distribution, increasing the interatomic separation R and thus reducing B . However an intermediate sized barrier, $\Phi' \approx 5B$, which favors an orientation of the molecule perpendicular to the surface inverts the splittings and can also give a para-ortho splitting of $\Delta_0 \approx B$.

We have also measured the separation coefficient for both H₂ and D₂ for our samples of activated alumina by allowing the adsorbed gas to convert to its equilibrium value at 20.4 K, desorbing, and measuring the ortho-para concentration by means of Raman scattering.¹⁰ The values obtained are 39^{+2}_-8 for H₂ and 5.0 ± 0.3 for D₂, strikingly different from earlier values for γ -Al₂O₃. A model-dependent S can also be determined from the neutron data of the count rate I versus energy transfer Δ :

$$\bar{S} = \int I S d\Delta / \int I d\Delta, \quad (4)$$

where the S used under the integral is given by Eq. (3). The uncertainty in such a determination is large because of the difficulty in interpretation of the scattering above and below the peak. If we include only the broad peak between 0.5 and $1.5B$ in Fig. 2(c), then we find $S = 86$ when we assume a transition to a doublet state or the 2-D rotor model and $S = 43$ if the transition is to a singlet state (1-D vibrator). If we include the total spectrum these numbers are $S = 160$ and $S = 80$, respectively.

In Table I we collect experimental data on the left-hand side and compare the various models on the right-hand side. The neutron data only exhibit one peak and thus the identification with barrier parameter Δ_0 or Δ_1 is model dependent. The

TABLE I. Experimental data and model results for the separation coefficient and energy splittings. $\Phi'/59.3$ is the ratio of the anisotropic barrier to the free-molecule B value of H₂.

Gas	Parameter	Present data		Ideal 2-D	Mod. 2-D	Model values		Neutron 1-D	Neutron 2-D
		Desorption	Neutron			Ideal 1-D	Mod. 1-D		
H ₂	S	39^{+2}_-8		43.8	39	1439	39	43	86
	Δ_1/Δ_0 (cm ⁻¹)		$52/\Delta_0$ or $\Delta_1/52$	$59.3/\infty$	$61/\infty$	$\infty/0$	184/52	-/52	52/-
	$\Phi'/59.3$	$-\infty$	$-\infty$		5.5
D ₂	S	5.0 ± 0.3		5.45	5.0	22.3	5.0
	Δ_1/Δ_0 (cm ⁻¹)		...	$29.9/\infty$	$31.1/\infty$	$\infty/0$	100/21
	$\Phi'/59.3$	$-\infty$	$-\infty$	∞	3.3

ideal 1-D and 2-D models can be rejected because of disagreement with the measured separation coefficients. A modified 2-D model in which $\Delta_0 = \infty$ and $\Delta_1 = B$ is a fitting parameter appears to give reasonable values of Δ_1 when fitted to the experimental value of S . However, this model can be rejected on the basis of the neutron measured line which requires a broad distribution for B , including unphysically small values as low as $0.6B$. Best agreement is found for a modified 1-D model in which the barrier Φ has an intermediate size. First, the width of the neutron peak can easily be understood in terms of a distribution of barrier heights $2.5 \leq \Phi'/B \leq 9$ [see Fig. 1(a)]. Second, fitting this model to the experimental values of S yields reasonable values of Δ_0 , Δ_1 , and Φ' . Third, the value of S determined by using the neutron intensities is close to the experimental value for the modified 1-D model whereas a 2-D model would be strongly excluded. Some objections to this model remain, namely the difference in Φ' found for H_2 and D_2 , and more importantly, the failure to identify the predicted high-energy transition in the neutron scattering. Within this model, one can use the observed neutron line to predict a broad line extending from 17 to 35 meV with a maximum at 23 meV and an integrated intensity double that of the low-energy transition. The broad unstructured scattering observed in this region could possibly arise from this and from translational motion which must also contribute to the intensity. The coupling of translational and rotational motion, not included in this model, could further broaden this transition. We point out that the conclusions we have drawn rest upon the assumption that the dependence of the adsorption potential $\epsilon(r_i)$ on the rotational states can be ignored.

In reality, the surface adsorption sites may be

pores with widths of the order of a molecular diameter.⁸ Further confirmation of the model presented can possibly be obtained from a number of different experiments including neutron scattering from hydrogen isotopes, rotational Raman scattering, temperature dependence of S , and NMR.

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