# HD and $D_2$ Layers Physisorbed on MgO Studied by NMR

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(Received 4 June 1992)

The D NMR spectra of HD and ortho $D_2$ are sensitive to the crystal fields from the MgO surface sites. At fractional coverages $0.6 < x < 0.9$, beyond the limit of island growth, rapid motion among inequivalent sites occurs, even at 4.2 K. For $1 < x < 2$, broad and narrow lines arise from the first and second layers, respectively. Isotopic bilayer mixtures show nearly complete separation, with the more massive specie in the first layer.

PACS numbers: 76.60.−k, 68.60.−p, 64.75.+g

We report a deuteron NMR study of HD and $D_2$ layers physisorbed onto MgO powder. The D line shapes provide unambiguous evidence of molecular motion in the compressed monolayer and reveal isotope separation in the bilayer. This information is essentially inaccessible by the more frequently employed thermodynamic and diffraction measurements. This particular system of hydrogen on MgO is an intriguing one, because of recent neutron scattering evidence [1] that multilayers retain a liquid component down to 7 K. Suppression of freezing to lower temperatures may result in a new superfluid [2].

The MgO substrate avoids many problems that the popular graphite substrate presents for NMR. The conductivity of graphite results in skin depth limitation of the rf fields, dictating use of low NMR frequencies and/or small samples, resulting in low sensitivity. Further, magnetism of the graphite, both natural and from impurities, makes interpretation of NMR results difficult [3]. The MgO for most of this work had specific area 30 $m^2/g$ and uniformity somewhat poorer than exfoliated graphite. A few experiments were performed on MgO prepared according to Coulomb and Vilches [4]. This material is much more uniform but has only 6 $m^2/g$. In both cases, a 1.25-$cm^3$ vessel held about 0.55 g of MgO powder.

The origin of spectral width is as follows: Free HD molecules have a $J=0$, nondegenerate rotational ground state. The spherical symmetry results in the vanishing of $\bar{P}_2 \equiv \langle 3\cos^2\theta - 1\rangle/2$, with $\theta$ the angle between the molecular axis and the external field. The interaction between the quadrupole moment of the D nucleus and the molecular electric field gradient is proportional to $\bar{P}_2$, as is the intramolecular proton-deuteron dipole coupling. Thus, in the $J=0$ state the D NMR spectrum of HD should be relatively sharp, broadened only by intermolecular dipole interactions of a few kHz. Thermal excitation of higher-$J$ states ($\geq 128$ K higher) is unimportant at the low temperatures of this work, $\lesssim 10$ K [5].

Deuteron spectra at 4.2 K and 8.3 T (54.4 MHz) for HD on MgO are presented in Fig. 1. The coverage $x=1$ corresponds to the start of second-layer formation. The first and most obvious feature of the data is the large linewidth ($\sim 30$ kHz) compared to that expected for $J=0$ molecules. Evidently the crystal field from the ionic MgO substrate [6] admixes higher-$J$ states into the rotational ground state [7]. The result is a rotational ground state that is not spherical. Thus $\bar{P}_2$ no longer vanishes and the quadrupole and intramolecular dipole interactions appear in the spectrum. The above explanation is supported by the following experimental observations. First, the spectra for $x > 1$ have a narrow component in addition to the broad component of $\sim 30$-kHz width. The intensity of the narrow component is nearly proportional to $x-1$, demonstrating that the narrow signal is from the second layer. The surface crystal field at the second layer should be much smaller than that at the first layer, so second-layer molecules should be in nearly pure $J=0$ ground states with narrow NMR lines, as observed. Second, the linewidths of the $x \leq 0.85$ spectra are in-

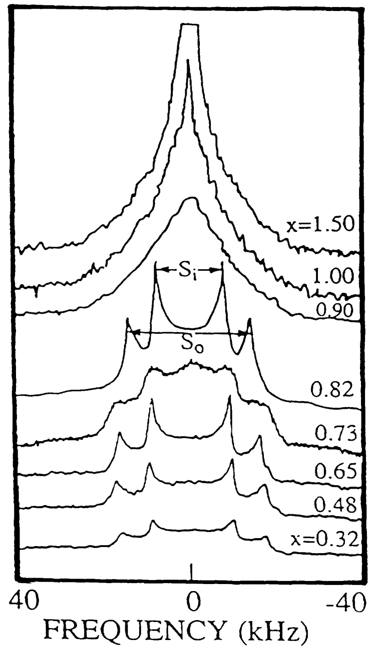

FIG. 1. Deuteron NMR spectra of physisorbed HD on MgO at 4.2 K. The coverage $x=1.00$ corresponds to the emergence of a sharp central line from second-layer molecules. The cusp-cusp splittings are marked on the $x=0.82$ spectrum. The sharp central component from the second layer of $x=1.50$ has been cropped. The gains of the spectra all differ; the signal to noise varies because of the varying numbers of signal averages.

dependent of temperature below 9 K, ruling out thermal excitation of higher-$J$ states.

The spectroscopic identification of first-layer and higher molecules reveals isotopic separations in mixtures. The D NMR spectrum at 4.2 K of $x=1.50$ layers of HD is presented in Fig. 2(a). Also presented is a spectrum of a mixture of $x=0.50$ HD with $x=1.00$ $H_2$. The two gases were admitted sequentially, the system was annealed for hours at 40 K, and the temperature was decreased. If the HD and $H_2$ occupied the two layers at random, the D signal would be the same shape as for the pure HD. Instead, the D signal (from HD only) exhibits only a broad component, demonstrating that all HD are in the first layer, closest to the MgO. Less than 1% of the HD is in the second layer, as the resulting sharp signal would be readily apparent in Fig. 2(a).

The isotopic separation of HD and $D_2$ is more difficult to infer because both species generate D NMR signals. Spin echoes from deuterons at 4.2 K are presented in Fig. 2(b). The pulse sequence is $90^\circ_x$-$\tau$-$90^\circ_y$, with $\tau=300$ $\mu$s and with data acquisition starting at the second pulse. The sample is $x=0.40$ HD plus $x=1.0$ $D_2$, annealed at 40 K before final cooling. In this time-domain data, the narrow echoes are associated with the broad frequency component and the first layer. The broad time feature is from second-layer molecules. The three narrow echoes evident in Fig. 2(b) are *multiple echoes* [8]. Essentially, because of interference between the quadrupole and intramolecular dipole couplings, the conventional $2\tau$ echo appears together with an earlier and a later echo. For ortho $D_2$, the echoes are expected [8] by calculation and experiment to appear at $1.85\tau$, $2\tau$, and $2.19\tau$. For HD, the times are $1.56\tau$, $2\tau$, and $2.78\tau$. Thus, multiple echoes allow HD and ortho $D_2$ to be unambiguously distinguished. Experimentally, the echoes appear only at the times expected for ortho $D_2$. Clearly, all the first-layer molecules are ortho $D_2$. We note that normal $D_2$ converts to ortho $D_2$ within 30 min on the MgO.

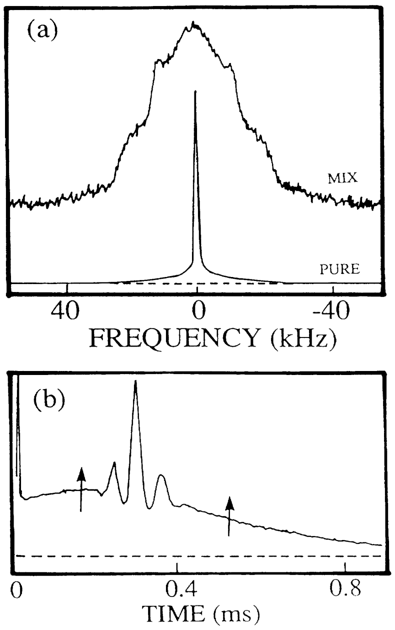

FIG. 2. (a) Deuteron frequency spectra at 4.2 K. An isotopic mixture of $x=0.50$ HD with $x=1.00$ $H_2$ is compared with a pure $x=1.50$ HD sample (displayed with much less gain, because of the sharp central line). The absence of a sharp central line in the mixture demonstrates that all HD are in the first layer. (b) Spin-echo deuteron signals at 4.2 K, in the time domain. The sample is $x=0.40$ HD plus $x=1.10$ $D_2$. The sharp echoes arise from the first layer, with the longer decay from second-layer molecules. The first and third echoes occur at the times expected for ortho $D_2$, while no such echoes are observed from HD (arrows). Thus the first layer is composed entirely of ortho $D_2$.

The isotopic separations displayed in Fig. 2 both result in more massive molecules in the first layer, as much as possible. This effect arises from the energy of zero-point motion. The only motions with substantial zero-point energy will be the high-frequency ones. In particular, the highest-frequency motion in the problem is expected to be the oscillation of a first-layer molecule normal to the surface, because this involves the largest binding energy (stiffest spring). For the quantum gases $H_2$, HD, and $D_2$, molecule-molecule interactions are much weaker than molecule-substrate interactions. In the resulting one-body problem, a molecule of mass $m$ is bound by energy $E=-V-\hbar\sqrt{k/4m}$. Here $-V$ is the classical binding energy and $k$ is the spring constant describing the potential well. Thus the heaviest molecules are bound most strongly, as observed.

For $x=1.5$ coverages of HD, we have observed layer-layer interchanges on the 10 s time scale at 5.6 K, using saturation transfer NMR experiments. Together with the $\gtrsim 10^4$ s time scale for cooling the isotopically mixed samples, this suggests that the samples were at equilibrium, ruling out kinetic explanations for the isotopic separation.

For coverages $0.08 \leq x \leq 0.85$, the D spectra are superpositions of two Pake powder doublets. The signals are Pake *doublets* because D is spin 1 and has two $\Delta m=1$ transitions. These are *powder* doublets because the sample contains surfaces at all orientations to the external magnetic field. There are *two* such patterns because the proton has two spin states. Essentially, in one spin state the quadrupole and intramolecular dipole couplings add; in the other state they subtract [8].

The cusp-cusp splittings $S_i$ and $S_o$, defined in Fig. 1, always yield $S_o/S_i=1.78\pm0.03$, in agreement with results for HD in amorphous silicon and with theory [8]. Thus the *ratio* $S_o/S_i$ is a molecular property, not a property of the adsorbed system. However, both splittings are proportional to $\bar{P}_2$, the deviation from sphericity of the rotational ground state. Specifically, one has

$$\bar{S}=(S_i+S_o)/2=(67.4\ \mathrm{kHz})\bar{P}_2/0.4\,.$$

Here $\bar{P}_2$ refers to the angle between the molecular axis and the surface normal. The factor of 0.4 enters because the 67.4 kHz value [9] refers to the $J=1$, $m=0$ state, for which $\bar{P}_2=0.4$. Thus, at a coverage $x=0.48$, we find $\bar{P}_2=0.15$ from the spectrum of Fig. 1. From perturbation theory, such a large value of $\bar{P}_2$ implies that the anisotropic potential for HD on MgO is not much smaller than the energy splittings between $J$ states (e.g., 128 K). This is quite different from that for ortho $H_2$ (odd $J$) on graphite, where small crystal fields (only ~1 K) were found [10,11], as confirmed by calculation [12]. Presumably the large electric field gradients from the ionic substrate [6] interacting with the $H_2$ molecular quadrupole moment are important.

We emphasize the following points. First, if all HD molecules occupy equivalent surface sites, the D NMR spectrum will be a *pair* of Pake doublets. Also, different adsorption sites with different crystal fields will result in different $\bar{P}_2$ values and different splittings $S_i$ and $S_o$. Hence, a distribution of adsorbtion sites will smear the sharp cusp features of the Pake doublets.

Above ~9 K the doublets disappear, with a single central line evident above 12 K. For the more uniform MgO of lower specific surface area, these temperatures are increased by ~4 K. At sufficiently low temperature the doublets smear for some coverages (see below). But at all concentrations from $x=0.08$ to 0.85, a substantial temperature-independent region appears.

The values of the splittings $S_i$ and $S_o$ at 7 K appear in Fig. 3. For $x \leq 0.60$, the splittings are constant to within our precision. This is the result expected for the island growth regime. In island growth, the *local* density in any patch is constant as the total coverage is varied; only the fraction of surface covered by patches varies. No phase diagram is available for submonolayer HD on MgO [13,14], but at the temperatures of this work one expects a 2D gas of negligible density to be in equilibrium with much denser patches.

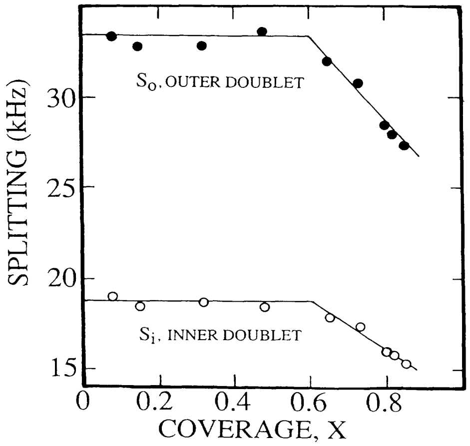

FIG. 3. Variation of the Pake splittings $S_i$ and $S_o$ with coverage $x$, all at 7 K. For $x \leq 0.6$, the constant splittings indicate island or patch growth. For $x > 0.6$, motional averaging over various adsorption sites is responsible for the splittings remaining sharp, though dependent on $x$.

HD molecules are expected to preferentially adsorb above Mg ions, because the HD can also make van der Waals contact with four neighboring, larger oxygen ions [15,16]. Mg sites are separated by 2.97 Å, too close to allow occupation of *every* Mg site by HD molecules of ~3.64 Å diameter (derived from the bulk HD molar volume [5] at 4.2 K and zero pressure). However, the commensurate $c(2\times2)$ structure [15] involves HD occupation of only half of the Mg sites, for an ideal density of 0.056 molecule/Å$^2$. The coverage $x=0.60$ (the limit of constant splitting; see Fig. 3) corresponds to a density of 0.061 molecule/Å$^2$, ±10%, as derived from a Kr isotherm at 77 K and an estimate of 0.0675 Kr/Å$^2$ at the 0.56-Torr substep [13]. The good agreement suggests that HD initially grows in islands with the commensurate $2\times2$ structure. In support, the spectra for $x \leq 0.60$ are double Pake doublets, indicating occupation of a *single* adsorption site, as is the case for $c(2\times2)$.

For $0.90 > x > 0.60$ the splittings in Fig. 3 vary with the coverage $x$. This indicates that the HD are increasingly forced to occupy sites with smaller crystal fields as $x$ increases. At the same time, the spectra retain their sharp, double Pake doublet appearance, provided the temperature $T$ is not too low ($T \geq 4.2$ K for $x=0.65$ and 0.82; $T \geq 6$ K for $x=0.73$). The sharpness of the Pake features demonstrates that all HD molecules are in the *same environment,* at least after averaging over times of order $10^{-5}$ s (the reciprocal of the intramolecular spin interactions). Starting with the $c(2\times2)$ structure, the only ways to increase the density involve interstitials, second-layer promotion, and higher-order commensurate or incommensurate structures. All of these involve *more than one surface environment* for the HD molecules. Thus, *motional averaging* over the inequivalent sites must be present to produce the sharp double Pake doublets. Because this motion is effective even at 4.2 K for $x=0.65$ and 0.82, the activation energy must be very low. Uniaxially incommensurate structures (commensurate in other direction) may occur for these coverages. In such a case, motion of discommensurations could result in the observed averaging.

Experimental support for the role of motions comes from broadening (smearing) of the Pake features as the temperature is reduced. For $x=0.73$ (see Fig. 1) this occurs already by 4.2 K. For $x=0.80$ and 0.82 the smearing occurs by 1.8 K. Thus motions responsible for spectral averaging are frozen out at low temperatures. At $x=0.48$ we have confirmed that cooling to 1.8 K does *not* cause the line shape to broaden, as expected for a commensurate structure of equivalent sites.

We note that high-order commensurate structures have been proposed to explain neutron diffraction data for $D_2$ on MgO [17]. For a nearly commensurate structure, an increased activation energy for motion of discommensurations is expected. This may be the cause of the broadening at comparatively high temperatures for the $x = 0.73$ coverage (Fig. 1). A thorough discussion of the rich phase diagrams of the hydrogens on graphite has appeared [18].

The featureless spectrum for $x = 0.90$ is shared by the broad component (first layer) of samples with $x \geq 1$. We understand these spectra as superpositions of double Pake doublets with a continuous distribution of $\bar{P}_2$ values and splittings. This describes an incommensurate layer of HD, but without any motional averaging. We note that $H_2$ and $D_2$ on graphite also exhibit high-density incommensurate phases, just before second-layer formation [19,20].

We gratefully acknowledge J. Z. Larese for supplying the MgO and for suggesting MgO as a more suitable substrate for NMR studies. We have benefited from discussions with O. Vilches, S. Fain, H. Meyer, and H. Wiechert, as well as M. Schick and M. Den Nijs. The work was supported by NSF Grants No. DMR 87-02847, No. 90-24502, No. 90-02857, and No. 91-03118.

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