NMR Study of the Orientational Behavior of Hydrogen Adsorbed on Graphite

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NMR has been used to study the orientational behavior of registered lattices of ortho-H_2 and para-D_2 molecules adsorbed on graphite in the range 1.3–4.2 K. The results show a weak crystal field (0.56 K for o-H_2 and 2.4 K for p-D_2). In addition, p-D_2 molecules experience a temperature-dependent molecular field arising from electrostatic quadrupole-quadrupole interactions. No orientational ordering occurs down to 1.3 K, a factor of 2 below the mean-field transition temperature.

We present here the first measurements of the orientational state of hydrogen molecules (H_2 and D_2) on a graphite substrate. At low temperatures and coverages below 65% of a full monolayer, hydrogen molecules adsorbed on Grafoil[1] are known to form a two-dimensional (2D) solid phase in registry with the graphite lattice.[2] Molecules are located at the center of every third carbon ring thereby forming a triangular lattice ($\sqrt{3}R\,30°$ structure). At 4.2 K and below, the ortho-para conversion rate is low enough ($\lesssim 0.5\%/\text{h}$) that the orientational states of the metastable $J=1$ hydrogen molecules (ortho-H_2 and para-D_2) can be studied by NMR.

The crystal field is found to be remarkably small and is substantially different for the two isotopes. Furthermore, for D_2 the effect of interactions between molecules is shown to follow a simple mean-field model with no evidence of long-range order down to 1.25 K, a factor of 2 below the mean-field transition temperature.[3] Such results are directly relevant to current theoretical work on critical phenomena in two dimensions.[3,4]

The orientationally dependent part of the potential of a hydrogen molecule contains two dominant terms involving the crystal field V_c and the electrostatic quadrupole-quadrupole (EQQ) interaction, respectively.[5] At high temperatures (a few K are sufficient) the latter are averaged out by molecular reorientation. For $J=1$ molecules, the crystal field is effectively axially symmetric about the normal to the basal plane of the Grafoil (z axis). This produces a temperature-independent energy gap $\Delta = V_c$ between the $m_J=0$ state and the doubly degenerate $m_J=\pm 1$ states. $V_c>0$ if the ground state has $m_J=0$.

We now show how Δ can be found from the temperature dependence of the splitting of the NMR spectrum. If transitions between $J=1$ sublevels are fast compared to the intramolecular interactions, then there are two NMR lines centered about the Zeeman frequency ν_0.[6] For an axial potential the NMR splitting $\delta\nu$ is given by

$$\delta\nu(T) = |\,3\sigma d(3\cos^2\beta - 1)|\,, \tag{1}$$

where

$$\sigma = \tfrac{3}{2}(p_0 - \tfrac{1}{3}). \tag{2}$$

β is the angle between $\vec{H}_0$ and the z axis, and p_0 is the fractional population of $m_J=0$ state. For o-H_2, d is the dipolar constant (57.67 kHz); for p-D_2, it is the sum of the dipolar constant (2.74 kHz) and the quadrupolar constant (22.50 kHz).[7] Thus, since p_0 is related to Δ by

$$p_0 = [1 + 2\exp(-\Delta/kT)]^{-1}, \tag{3}$$

we can determine Δ from $\delta\nu(T)$.

Most of the work was done using a sample consisting of 0.28-mm-thick Grafoil sheets interleaved with 0.013-mm sheets of Teflon to reduce rf shielding. The sheets were parallel to both the rf field $\vec{H}_1$ and the axis of the quartz tube[8] containing them as shown in Fig. 1(a). The sample was pressed tightly into the quartz tube. Nevertheless some rf heating of the Grafoil was present at the lower temperatures. A small correction to the sample temperature was made using the T^{-1} dependence of the intensity of the narrow o-D_2 resonance.

The Grafoil was initially baked under vacuum at 900°C. After constructing the sandwich in air the NMR wand was baked at 200°C and vacuum was maintained thereafter. A second sample with the Teflon replaced by 0.1-mm single-crystal sapphire was activated *in situ*, but gave identical NMR signals to the sample with Teflon.

The surface area of the Grafoil was calibrated using the helium vapor-pressure isotherm. The wand, containing a known quantity of hydrogen (~2 cm^3 at STP), was lowered over a period of about 15 min into a liquid helium bath while monitoring the pressure above the substrate. Adsorption was performed relatively quickly because ortho-para conversion is much faster during this process than when the sample is in the solid phase

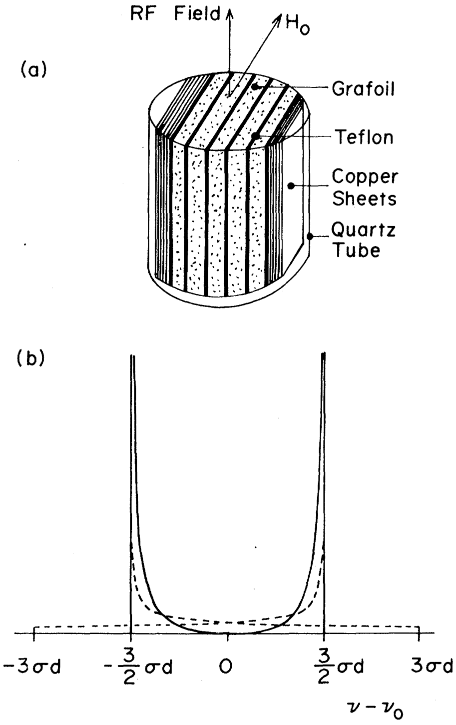

FIG. 1. (a) The NMR sample. (b) Unbroadened NMR line shapes for a powder (dashed) and a sheet of Grafoil with $\vec{H}_0$ parallel to the sheet (solid). The two curves are normalized to the same area.

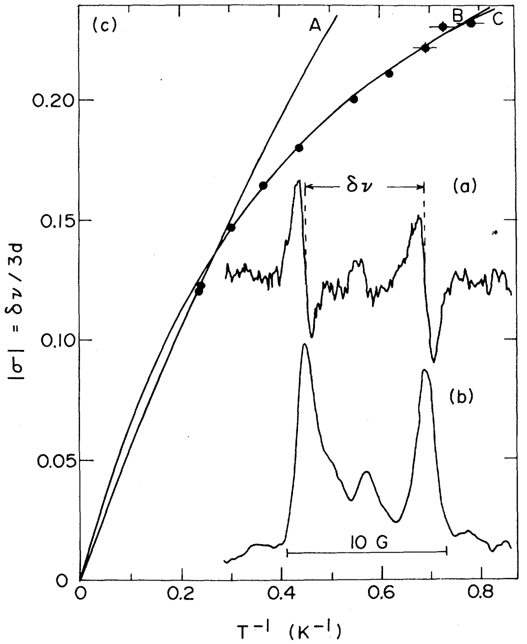

FIG. 2. (a) Derivative of the NMR absorption signal of 92% p-D_2 at 4.17 K with 80% of full coverage in the $\sqrt{3}R30°$ phase. (b) Integral of (a). (c) $|\sigma|$ vs T^{-1} for 92% p-D_2.

at 4.2 K. Immediately after each run the ortho concentration was analyzed by comparing the intensities of the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ Raman lines. Final concentrations of 92% p-D_2 and 93% o-H_2 have been achieved using an initial purity of >98%.

Conventional derivative NMR spectra were obtained with an 8.8-MHz Robinson oscillator employing a liquid-helium-cooled preamplifier. Typically 1–2 h of signal averaging were used.

The NMR splitting is given by Eq. (1). Neglecting broadening, one gets two δ-function lines for a single crystal. For a powder sample one must average over all solid angles resulting in the dashed curve of Fig. 1(b).[9] In a sheet of Grafoil the basal planes have an angular distribution with a full width at half-maximum of 27°.[2] If $\vec{H}_0$ is parallel to the sheets (as in our case), one gets the solid curve of Fig. 1(b).

Figure 2(a) shows the derivative of the NMR absorption for 92% p-D_2. Figure 2(b) is the integral of Fig. 2(a). The central line is due to the o-D_2 molecules ($I = 2, 0$) and the two outer lines are due to p-D_2 ($I = 1$). Broadening arises primarily from both the angular distribution of the basal planes and the anisotropic diamagnetism of the Grafoil.[10]

Figure 2(c) shows the absolute value of the order parameter $|\sigma|$ as a function of inverse temperature. The data were obtained from the splitting $\delta\nu$ of the $J = 1$ absorption peaks using Eq. (1) with $\beta = \pi/2$ so $|\sigma| = \delta\nu/3d$. Curve A is a fit to the high-temperature data using an adjustable temperature-independent energy gap $\Delta = V_c$; EQQ interactions were ignored. Negative values of V_c give a better fit at low temperatures; positive values are equally good at high temperatures since there $\delta\nu$ does not depend on the sign of σ.

Clearly the use of a temperature-independent energy gap Δ is unsatisfactory. If the EQQ interaction is included using molecular-field theory, then for a pure system of $J = 1$ molecules in the absence of long-range order, the energy gap becomes temperature dependent[3]:

$$\Delta = V_c - \tfrac{27}{2}\Gamma\sigma(T). \qquad (4)$$

Γ is the quadrupole coupling constant for hydrogen on Grafoil. By solving Eqs. (2)–(4) simultaneously one obtains the temperature dependence of the order parameter σ. Curves B and C of Fig. 2(c) are least square fits to the data using two parameters V_c and Γ. The former has $V_c = -2.4$ K and $\Gamma = 0.47$ K whereas the latter has $V_c = 2.3$ K and $\Gamma = 0.50$ K. A fit using one parameter (V_c) with Γ fixed at its value for a rigid lattice (0.580 K) is almost as good. It is not unreasonable to expect some renormalization of Γ due to zero-point motion. Harris[5] has shown that for 3D solid hydrogen in the disordered hcp phase, Γ is renormalized down by 13% for o-H_2 and 12% for p-D_2.

For 93% o-H_2 the NMR splitting cannot be resolved at 4.2 K because of intermolecular dipolar broadening. By using 21% o-H_2, the splitting can be resolved as can be seen in Figs. 3(a) and 3(b), but dipolar broadening remains dominant.

Figure 3(c) shows $|\sigma|$ as a function of T^{-1}. Curve A is a one-parameter (V_c) fit for $V_c > 0$ with Γ fixed at its unrenormalized value of 0.626 K. Negative crystal fields give a slightly worse fit. The optimum two-parameter fits, $V_c = -0.56$ K with $\Gamma = -0.07$ K and $V_c = 0.56$ K with $\Gamma = 0.13$ K, both yield curve B. A fit with $V_c = \pm 0.56$ K and $\Gamma = 0$ is essentially linear in this range and very similar to curve B. The quadrupole interaction has apparently been renormalized almost to zero for o-H_2. This may be because H_2 has larger zero-point motion than D_2.

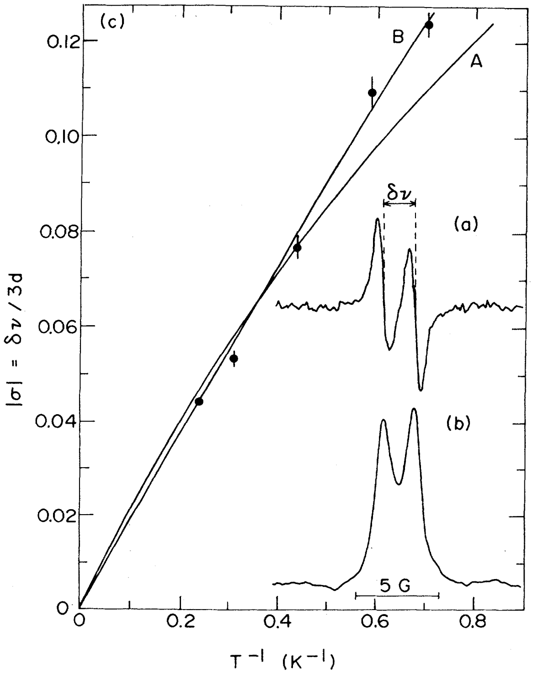

FIG. 3. (a) Derivative of the NMR absorption signal of 21% o-H_2 at 4.21 K with 85% of full coverage in the $\sqrt{3}R30°$ phase. The background has been subtracted. (b) Integral of (a). (c) $|\sigma|$ vs T^{-1} for 21% o-H_2.

These measurements cannot separate contributions to the crystal field from the substrate and from neighboring hydrogen molecules. Theoretical estimates of the two effects can be made, though. Following Raich and Kanney,[11] the hydrogen contribution is

$$V_c^{H} = -\tfrac{3}{5} {\sum_{j\neq i}}' B(R_{ij})(3\cos^2\theta_{ij} - 1). \tag{5}$$

θ_{ij} is the angle between $\vec{R}_{ij}$ and the z axis and $B(R_{ij})$ is the potential between two hydrogen molecules separated by $\vec{R}_{ij}$. Raich and Kanney fit the potential to the form

$$B(R) = Ae^{-\alpha R} - cR^{-6}. \tag{6}$$

With their parameters and $\theta_{ij} = \frac{1}{2}\pi$, one find $V_c^H = -1.90$ K for H_2 on Grafoil. The results for D_2 should be very similar. The attractive long-range term of the potential is a factor of 3 larger than the short-range term.

The substrate contribution to the crystal field V_c^s has been estimated[12] by summing over the interactions of a $J = 1$ hydrogen molecule with individual C atoms. Assuming the C atoms to be spherically symmetric, we take the pair interaction to have the form

$$V(\rho, \theta) = [1 + \gamma P_2(\cos\theta)]U(\rho), \tag{7}$$

where $\vec{\rho}$ is the vector between the centers of mass, θ is the angle between $\vec{\rho}$ and the hydrogen internuclear axis, P_2 is a Legendre polynomial, and U is the Lennard-Jones potential. The sum of the pair interactions can be represented as a Fourier series in the position variables of the hydrogen molecule in the plane parallel to the graphite surface.[13] If we retain only the uniform component and replace the sum over all lattice planes except the first by an integral [Eq. (3.1) of Steele (Ref. 13)], then one gets $V_c^s \sim 9$ K.

The total crystal field is then $V_c \sim 7$ K, which is considerably larger than the experimental values of $|V_c|$ for p-D_2 (2.3 K) and o-H_2 (0.56 K). Because of the uncertainties in the theoretical calculations, they may not be inconsistent with a value of $V_c = 2.3$ K for D_2, though it is hard to reconcile them with the experimental results for o-H_2 or a negative crystal field for D_2.

Using mean-field theory, Berlinsky and Harris[3] have determined the orientational phase diagram of $J = 1$ hydrogen molecules on a triangular lattice. With the values of V_c and Γ obtained from our p-D_2 NMR data, their theory predicts for pure p-D_2 a second-order phase transition to an ordered four-sublattice structure at 2.5 K if $V_c > 0$ and a second-order transition to an ordered two-sublattice structure at 3.3 K if $V_c < 0$. The

NMR data show no evidence of a transition down to 1.25 K. It is clearly of interest to extend the experiment to lower temperatures in order to determine whether ordering actually takes place or whether fluctuations in this 2D system reduce the transition temperature to zero.

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Threshold for Optically Induced Dislocation Glide in GaAs-AlGaAs Double Heterostructures: Degradation via a New Cooperative Phenomenon?

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We have observed a sharp threshold for the process of optically induced glide at which the velocity changes by more than a factor of 10^3 when the excitation intensity changes only 20%. This threshold is insensitive to doping and to the presence of a *p-n* junction. The effect is shown not to be related to recombination-enhanced motion or to local heating. An explanation in terms of the reduction of frictional forces by interaction with unrecombined carriers is offered.

It has been reported previously[1,2] that optical excitations of intensity in excess of 10^5 W cm^{-2} can lead to rapid (50 μm s^{-1}) dislocation glide in AlGaAs double-heterostructure lasers. The observations were made using photoluminescence topography. A laser wafer, without the normal capping layer of GaAs, is illuminated by the focused 647.1- and 616.4-nm radiation of a Kr^+ laser, to which the upper waveguide layer is transparent but the active layer is not. The active layer may be observed by the photoluminescence produced in it. Defects are apparent as dark regions because of the higher probability of nonradiative recombination events in their vicinity. Thus the motion of a gliding dislocation may be observed directly as a moving dark spot in the photoluminescence field.

The glide process does not occur at dislocations which were present during growth, but only at fresh dislocations. These are introduced by gently scratching the surface of the upper waveguide layer. On applying an optical excitation of sufficient duration, a dense dislocation network develops within a few microns of the scratch. Similar networks have been observed in studies of moderate-intensity 10.6-μm-laser damage in GaAs.[3]

A secondary stage of damage may now be produced if the optical excitation is sufficiently intense. Then we find that dislocation loops will glide away from the damaged area. This results in a portion of the dislocation threading from the bottom waveguide layer through the active layer and the upper waveguide layer to the surface.