serve that T_0 varies between 8 and 40 K. When reasonable values[6] of $\alpha^{-1} \approx 100-500$ Å and $N_2 \leq 1.6 \times 10^{14}$ eV^{-1} cm^{-2} are inserted in these expressions, it is found that w is typically 200–500 Å and w/R is typically 0.1–0.5. Thus this explanation is at least plausible, given the approximations.

In the Coulomb-gap model[7] $T_0 = 8\alpha e^2/\kappa k_B$, where κ is the dielectric permittivity of the Si. When the full Coulomb potential is used to determine T_0, it is found that $T_0 = 280$ K. Thus for the Coulomb-gap argument to obtain the Coulomb potential would have to be reduced by a factor of about 10. The Coulomb-gap theory therefore would seem to be inconsistent with our data.

It has been theoretically shown[8] that simply activated behavior ($n = 1$) should be observed in a one-dimensional chain because there are no percolation paths and one large barrier will control the current. It has been argued[9,10] that in short enough samples no such blockades exist and that the $\ln\sigma \approx (T_0/T)^{1/2}$ law obtains. We are not convinced that the last theoretical word has been heard on this subject. Other experimental results[11] also seem to give $n = \frac{1}{2}$ for chains or narrow samples.

We do not have a plausible explanation as to why strong localization persists to such high values of N_S or gate voltage in these dimensionally restricted samples, even when they follow a two-dimensional variable-range hopping law. These samples do not lend themselves easily to a solution of Poisson's and Schrodinger's equation, so that no simple model is at hand for the induced electron distribution in the accumulation layer. While we cannot argue conclusively that a transition from one-dimensional variable-range hopping to two-dimensional variable-range hopping explains these results, we favor this explanation as the simplest and most plausible.

We would like especially to acknowledge conversations with M. Pepper, who first conceived of this type of sample, with M. Pollak, and with R. Isaac and J. Blum who helped us immeasurably with the process design of the samples.

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Observation of Rotational Excitations of H_2 Adsorbed on Ag Surfaces

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High-resolution electron-energy-loss studies of H_2 on Ag at ~ 10 K reveal both rotational and rotational-vibrational excitations of molecularly adsorbed and condensed H_2. The rotational losses for submonolayers of adsorbed H_2 indicate unhindered rotational motion as well as a H-H internuclear separation which is within ~ 2% of that of condensed H_2. Adsorbed H_2 is also converted from predominantly orthohydrogen to parahydrogen.

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Several recent theoretical studies[1-5] have considered the interaction of molecular hydrogen with a metal surface. These studies have investigated the nature of bonding for a variety of metal-molecule bonding distances and molecular orientations, as well as the mechanisms of dissociation to form atomic hydrogen. Despite hydrogen's apparent role as a simple theoretical prototype adsorbate, relatively little direct experimental information exists for comparison or for insight to such questions. Here, we report high-resolution electron-energy-loss studies of molecularly adsorbed and condensed H_2 on Ag films and a Ag(111) surface which provide new information as to the nature of bonding of adsorbed H_2, the H-H internuclear separation, and the nuclear spin state of the adsorbed molecule on Ag. Our study is also significant in that this is the first observation of rotational and rotational-vibrational excitations for any molecule adsorbed on a metal surface. These rotational excitations provide us with novel information and new insight to this adsorption problem not previously possible.

These experiments were performed in an ion- and sublimation-pumped UHV system (base pressure 6×10^{-11} Torr) which contains a hemispherical deflection-analyzer-based, high-resolution, electron-energy-loss spectrometer which is described elsewhere.[6,7] For these experiments we have selected an incident electron beam energy of ~3 eV so as to obtain strong rotational excitations of H_2, as are well known to occur from gas-phase impact studies.[8] Ag films were evaporated *in situ* from a tantalum boat onto a copper block which could be cooled by liquid He. An Ag(111) surface, prepared by standard mechanical and chemical polishing, was later mounted directly to the copper block where it could be sputter cleaned and annealed to ~200 °C. Both samples could be cooled to temperatures low enough to condense thick layers of H_2 ($T\sim 10$ K). The copper block could not be rotated and was oriented ~3° from specular scattering conditions, giving $\theta_i\sim 42°$ and $\theta_0\sim 48°$. This fixed sample position prevented optimization of the electron optics and thereby limited our resolution to 12 meV. Sample dosing was done via the chamber ambient and was directly monitored by an ion gauge. The exposures cited are in langmuirs (1 L = 10^{-6} Torr sec) and have been corrected for the gauge correction factor of 0.45 for H_2 and 0.4 for D_2.

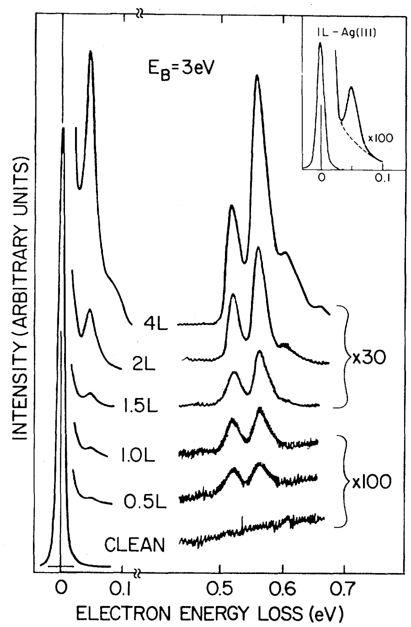

FIG. 1. Electron-energy-loss spectra as a function of H_2 exposure in langmuirs (1 L = 1×10^{-6} Torr sec) to a silver film held at ~10 K. Off-specular scattering conditions are used ($\theta_i\sim 42°$, $\theta_0\sim 48°$) and the low-energy region has not been enlarged relative to the scale settings for the clean surface. The higher-energy-loss scale magnifications are indicated. A magnified version of the low-energy-loss feature for Ag(111) is shown in the inset.

In Fig. 1 we show the electron-energy-loss spectra of H_2 on clean Ag surfaces as a function of exposure. Up to 1-L exposure the spectra are characterized by loss peaks at 49, 518, and 562 meV. For exposures above 1 L the intensities of the loss features increase significantly with exposure and the loss peaks shift slightly to 46, 515, and 557 meV (at 4 L). These spectral changes suggest the completion of monolayer adsorption at 1 L and a near-unity sticking coefficient. These spectra can be directly compared to both the gas-phase[9,10] and condensed-phase[11,12] Raman and ir spectra of p-H_2 which show strong transitions at 44, 514.5, and 556.2 meV. These transitions correspond to the pure rotational $J''=0\rightarrow J''=2$ transition, $S_0(0)$; the vibrational $v=0\rightarrow v=1$, $J''=0\rightarrow J'=0$ transition, $Q_1(0)$; and the $v=0\rightarrow v=1$, $J''=0\rightarrow J'=2$ rotational-vibrational transition, $S_1(0)$, respectively. The 4-L spectrum also shows other weak features such as a shoulder at ~70 meV and peaks at 607 and 650 meV. The weak 70-meV feature can be assigned to the $J''=1\rightarrow J''=3$ rotational transition of o-H_2, while the other peaks correspond to multiple loss features as observed in the condensed phase.[11,12]

As previously mentioned, we believe that submonolayer molecular adsorption, i.e., adsorption directly onto the surface, occurs until ~1-L exposures. We observe no unusual coverage or time-dependent spectral features in the monolayer regime (0.2–1 L) which would suggest preferential bonding at defect sites or grain boundaries of our polycrystalline film, or molecular dissociation. We also find that monolayer adsorption of H_2 on Ag(111) shows the same loss features and comparable intensities as found on the Ag films. A portion of the loss spectra for a 1-L exposure of H_2 to Ag(111) is shown in the inset of Fig. 1.

In Fig. 2, we show electron-energy-loss spectra for D_2 on Ag. Again, similar features are ob-

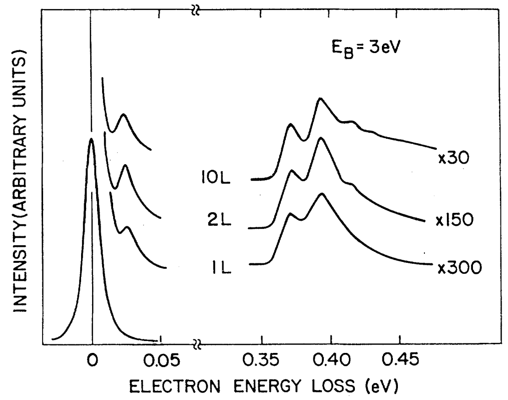

FIG. 2. Electron-energy-loss spectra as a function of D_2 exposure to a silver film as per Fig. 1.

served as for H_2. The low-energy transition at 25 meV is at ~$\frac{1}{2}$ the energy of the corresponding H_2 transition, while the next loss appears at 372 meV, i.e., at ~$1/\sqrt{2}$ the energy of the corresponding H_2 transition. This is the expected behavior for a rotational and a vibrational transition, respectively. The close correspondence of the spectra of adsorbed H_2 with the spectra of the gaseous and condensed H_2, as well as the observed isotopic shifts, demonstrates that we observe molecular rotation in the adsorbed phase.

In gaseous or condensed H_2 the rotational motion is characteristic of a three-dimensional (3D) rigid rotor. In this case, the rotational energy is given by $E_r = B_0 J(J+1)$,[13] where J is the rotational quantum number and B_0, the rotational constant. $B_0 = \hbar^2/2I$, and depends only on I, the moment of inertia: It does not depend on the nature or quantization of the rotations. For the 3D rotor the first allowed rotational transition ($\Delta J = 2$) occurs at $6B_0$, where for free H_2, $B_0 = 7.35$ meV.[9] For a two-dimensional (2D) rigid rotor the quantization differs and leads to different rotational energies, $E_r = B_0 m^2$, where $m = 0, \pm 1, \pm 2, \ldots$.[14,15] In the 2D rotor the lowest transition occurs at $4B_0$. Our measured rotational energies of 46–49 meV agree with those expected of the 3D rotor indicating that the rotations are *not* restricted to the plane of the surface. This "unhindered" rotational motion implies that any surface-derived potential barrier for rotation must be $\leq B_0$.[15]

From our observed rotational frequencies we can also determine the H-H internuclear separation, r_e, since the 3D rotor equations contain the moment of inertia $I = \mu r_e^2$, where μ is the reduced mass. For H_2 adsorbed directly on Ag we obtain $r_e = 0.70$ Å and for our thickest condensed layers we obtain $r_e = 0.72$ Å. This can be compared to the known r_e for gaseous or condensed H_2 of 0.7416 Å.[13] As a result of several experimental uncertainties in determining an absolute value for E_r, our r_e values could be uncertain by as much as 0.02 Å. However, the relative values for adsorbed and condensed H_2 can be more accurately compared and they suggest a small (~0.02 Å) contraction of r_e for adsorbed H_2 relative to condensed H_2. A similar contraction of the H-H internuclear distance has been observed at high pressures prior to solidification.[16] Possible renormalization of the rotor mass of adsorbed H_2, associated with coupling to the metal, would tend to increase μ (Ref. 17) so as to require a larger contraction to explain our data.

Recent theoretical calculations[1,3] of the adsorption of H_2 on metals predict the existence of two molecularly adsorbed H_2 phases prior to dissociation. One molecular phase, referred to as chemisorbed, occurs at "small" metal-molecule distances and is characterized by a parallel bonding geometry (H-H axis parallel to the surface) and a slightly expanded (~10%) internuclear separation from that of gaseous H_2. At larger metal-molecule distances (e.g., ~7 a.u. for H_2 on Mg)[1] a more weakly bound state of physisorbed H_2 is predicted. It is likely that we are observing such a physisorbed molecular state since we find unhindered 3D rotations and no evidence for H-H bond expansion. A physisorbed phase of H_2 being far from the surface atoms would also be least likely to feel the details of the surface crystallography. This may account for the similarity of our results on both the film and single-crystal surfaces. Further, our observation of unhindered rotations provides a measure of the orientational barriers ($\leq$ 7 meV) experienced by this physisorbed molecule as well as further evidence for the high mobility of physisorbed hydrogen on metals.[18]

Our results also directly allow us to determine the nuclear spin state of adsorbed H_2. Specifically, as a result of the Fermi-Dirac statistics, the para- and ortho-nuclear spin forms of H_2 will only exist in even or odd rotational states, respectively.[8,13] As mentioned earlier, our data indicate that H_2 in the adsorbed phase is in the $J = 0$ rotational level, i.e., in the para form. Since the impinging H_2 gas is at room temperature and is mostly o-H_2 ($J = 1$),[19] spin conversion occurs upon adsorption or within the 1–2 min of our initial exposures (i.e., the time required for dosing and running our spectra). In comparison, the conversion in bulk condensed H_2 is significantly slower, i.e., ~6% per hour with complete conversion occurring over a period of weeks![15] For our thickest condensed layers (10 L) the conversion is slower than for the first adsorbed layer and we can initially observe more o-H_2 than observed in Figs. 1 and 2. This suggests that the conversion of orthohydrogen to parahydrogen likely involves a short range (magnetic) interaction of molecular H_2 with the metal surface. Clearly, this conversion process remains to be more completely understood.

In summary, we have observed pure rotational and rotational-vibrational excitations of H_2 and D_2 adsorbed on Ag at ~10 K. Our results show unhindered rotations and an internuclear separation slightly shorter but within 2% of the condensed phase. This provides evidence for a physisorbed state which does not feel the anisotropies or energy barriers along the surface. The adsorbed H_2 has also been converted to the paranuclear spin state.

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Magnetic Energy Fluctuations: Observations by Light Scattering

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The first observations of magnetic energy fluctuations by light scattering are reported. The spectra observed in antiferromagnetic $KNiF_3$ are strongly polarized, mildly q dependent, but strongly temperature dependent near $T_N = 248.5$ K. The observed line shapes exhibit two characteristic frequencies, one less than 0.6 GHz and the other between 5 and 15 GHz, depending on temperature.

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Inelastic light scattering in magnetic solids has traditionally been employed to measure the behavior of spin waves and of spin-wave pairs with near-zero total momentum.[1] From such measurements accurate values for parameters in the spin Hamiltonian of ferromagnets, ferrimagnets, and antiferromagnets have been obtained.[2,3] In addition to these effects, it should in principle be possible to observe directly the fluctuations in the spin-wave density, or the magnetic energy, through a process analogous to the phonon density fluctuation scattering recently proposed and observed in phonon systems.[4]

In this Letter we report the first observations by light scattering of this type of process. As shown in Fig. 1, the light scattering spectra, ob-