PHYSICAL REVIEW B VOLUME 27, NUMBER 1 1 JANUARY 1983

Trapping of molecular hydrogen at surfaces via translational-rotational energy conversion

S. Andersson
Department of Physics, Chalmers University of Technology, S-412 96 Göteborg, Sweden

J. Harris
Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

(Received 24 June 1982; revised manuscript received 13 September 1982)

Using electron-energy-loss spectroscopy (EELS) intensities of rotational transitions and work-function changes as monitors, we show that molecular hydrogen gases, thermal ortho-para H_2 mixture, para-H_2, D_2, and HD, adsorbing on a cold Cu(100) surface have different sticking coefficients. The relative sticking coefficients and the relative populations of ortho- and para-H_2 on the surface, as estimated by EELS, can be understood on the basis of a trapping mechanism involving conversion of center-of-mass kinetic energy into rotational energy.

I. INTRODUCTION

When a particle from the gas phase adsorbs at a cold surface its initial kinetic energy ϵ_i as well as the adsorption energy ϵ_a must be dissipated. Dissipation does not generally occur via a single event, and it is usual to focus on the "trapping" of the particle in a high-lying, but bound level of the adsorption potential well. It is assumed that provided the surface is cold enough, the majority of the trapped particles will not revert to the gas phase but will stick permanently. If the surface is only weakly corrugated, as in the case we consider presently, most collisions will conserve parallel momentum so the trapping step requires dissipation not of energy ϵ_i, but of the normal component $\epsilon_i^z=\epsilon_i\cos^2\theta_i$, where θ_i is the angle of incidence. Most theoretical discussions of the sticking problem amount to calculations of the probability that phonons or electron-hole pairs carry away energy ϵ_i^z during the first "round trip" of the particle in the well.[1]

In this paper we report measurements of the sticking coefficient of H_2 molecules on a cold Cu(100) surface that are not easily reconciled with this point of view. Specifically, we show that H_2 gases which differ only in their rotational populations have different sticking coefficients. This implies that molecules having the same incident energy and angle but which are in different rotational states have different sticking probabilities. To explain this observation in terms of direct excitation of phonons or electron-hole pairs would require that the excitation probability depends strongly on the rotational state of the molecule. This is possible, but seems unlikely. As an alternative, we propose a mechanism involving simultaneous excitation of the solid and rotational excitation of the molecule. The normal kinetic energy ϵ_i^z is converted primarily into a rotational excitation of the molecule, with only a small part carried away as phonons or electron-hole pairs. We will show that the relative sticking coefficients for H_2 gases with different rotational populations, as well as those of H_2 and D_2 gases, can be explained simply as a consequence of this mechanism.

II. EELS AND WORK FUNCTION MEASUREMENTS

In a recent letter[2] we reported electron-energy-loss spectroscopy (EELS) measurements which established that (i) H_2 physisorbs on a cold ($\sim$10-K) Cu(100) surface and (ii) physisorbed H_2 displays well-defined rotational and rotational-vibrational excitations at energies virtually identical to the gas-phase values. This indicates that the potential energy of molecules in low-lying levels of the physisorption well is practically independent of the orientation and internuclear separation of the molecule, i.e., that the coupling between center-of-mass and relative motion is weak. A recent calculation of the potential energy in the region at and near the well minimum gave the same result.[3] The weakness of the coupling is due in part to a cancellation between the van der Waals attraction, which favors an orientation of the molecule normal to the surface, and the repulsive branch, which favors a parallel orientation.

EELS spectra obtained following adsorption to saturation of two H_2 gas, n-H_2, and p-H_2, differing only in their distributions of rotational levels, are shown in Fig. 1. Experimental conditions and details concerning the cleaning of the Cu(100) surface and on sample cooling were given previously.[2] Both

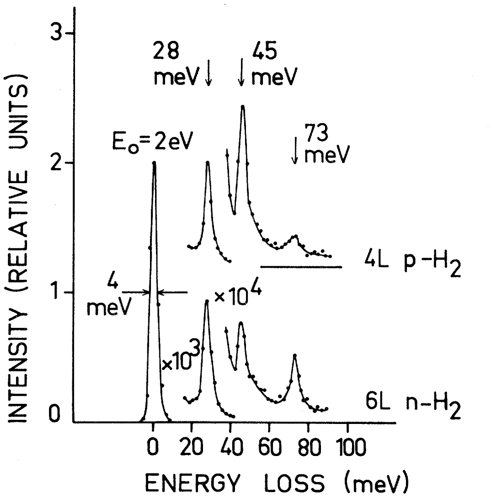

FIG. 1. Electron-energy-loss spectra from saturated monolayers of n-H_2 and p-H_2 adsorbed on Cu(100) at 10 K (1 L $=1\times10^{-6}$ Torr sec). The spectra were measured in specular direction for an angle of incidence 50° and energy 2 eV of the incident-electron beam.

gases display three features, at 28, 45, and 73 meV, the first of which is due to trace amounts of discreetly adsorbed H_2O molecules ($\theta<0.01$).[4] The features at 45 and 73 meV are due, respectively, to the $j=0\rightarrow2$ and $j=1\rightarrow3$ rotational transitions of physisorbed H_2. The EELS lines are quite sharp, indicative of long-lived excitations and the occurrence of two transitions shows that there is negligible coupling between even- and odd-j rotational levels. Both ortho- and para-H_2 exist on the surface in rotational states $j=1,0$, respectively, with negligible conversion on the time scale ~30 min. This reflects the absence of a mechanism on the surface for flipping a nuclear spin.

Though both n-H_2 and p-H_2 give rise to rotational peaks at the same energies, the relative intensities of the $j=0\rightarrow2$ and $j=1\rightarrow3$ lines are different in the two cases, reflecting the differing rotational populations of the incident gases. n-H_2 was a thermal mixture ($T_g=290$ K) having relative populations in rotational states $j=0,1,2,3$ of $n_j=0.13,0.67,0.11,0.08$, respectively. The p-H_2 gas, predominantly para-hydrogen (even j), was prepared by flowing n-H_2 over a nickel-silicate catalyst kept at 25 K.[5] Raman spectral analysis showed an ortho-para ratio of <0.1, as compared with the thermal value of 3. However, the ortho-concentration increased somewhat when the gas was leaked into the chamber, presumably because interaction with the chamber and ion-pump walls gives rise to exchange with normal H_2 and perhaps some back conversion. That p-H_2 is predominantly para is clear from the strong $j=0\rightarrow2$ 45-meV peak evident in Fig. 1. The small concentration of ortho-H_2 gives rise to a weak, but well-resolved $j=1\rightarrow3$ 73-meV peak.

In Ref. 2 we pointed out that the relative strengths of the $j=0\rightarrow2$ and $j=1\rightarrow3$ transitions for n-H_2 do not follow directly from the ortho-para ratio of the incident gas. From the spectra, we estimate

$$\left.\frac{I_{1\rightarrow3}}{I_{0\rightarrow2}}\right|_{n\text{-}H_2}=0.80\ . \tag{1}$$

To convert this figure into a population ratio for molecules adsorbed in rotational levels having $j=1$ and $j=0$, we must take account of the different EELS cross sections. In view of the weakness of the coupling between molecule and surface we expect the *relative* cross sections (though not necessarily the absolute cross sections) to be the same as in the gas phase, i.e., $\sigma_{1\rightarrow3}/\sigma_{0\rightarrow2}=0.6$.[6] Combining this with Eq. (1), we estimate a population ratio for n-H_2 of

$$\left.\frac{P_1}{P_2}\right|_{n\text{-}H_2}=1.3\ . \tag{2}$$

A similar analysis for the p-H_2 gas gave the estimate

$$\left.\frac{P_1}{P_0}\right|_{p\text{-}H_2}=0.2\ . \tag{3}$$

If the sticking probability for H_2 is independent of the rotational state, the ratio of populations given in (2) must be 3.0. Since we saw no reason to distrust the value quoted above for the relative EELS cross sections, and in view of the negligible ortho-para conversion for physisorbed molecules, we concluded in Ref. 2 that the sticking probability of H_2 on Cu(100) is *not* independent of the gas-phase rotational state. This conclusion we have since confirmed, as we now discuss.

Figure 2 shows how the intensities of the 45-meV $j=0\rightarrow2$ and the 73-meV $j=1\rightarrow3$ EELS lines depend on the n-H_2 exposure. The intensity increases linearly and saturates abruptly at about 6.5×10^{15} mol/cm^2 exposure.[7] The EELS spectra grow in smoothly during exposure and the ratio of intensites remains constant within experimental accuracy. As a second monitor of the adsorption kinetics we show in Fig. 3 the work function change $\Delta\phi$ during adsorption, measured using the EELS instrument as a retarding analyzer. For n-H_2, $\Delta\phi$ decreases linearly[8] and saturates abruptly, mirroring the behavior of the EELS intensities shown in Fig. 1. The linear dependence of $\Delta\phi$ on exposure is strong evidence that only one monolayer of H_2 forms. If the H_2 were condensing in layers, we would expect each layer to have a different effect on the work function, whose

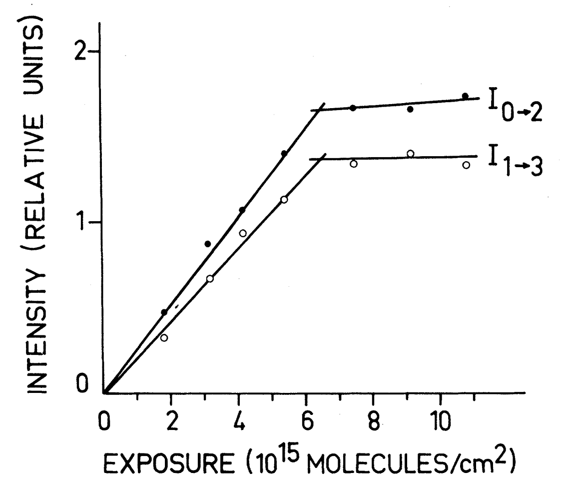

FIG. 2. EELS intensities of the 0→2 (●) and 1→3 (○) rotational transitions vs exposure for n-H_2 adsorbed on Cu(100) at 10 K. Experimental parameters as in Fig. 1.

dependence on exposure would therefore be nonlinear.

Also shown in Fig. 3 are the work-function changes that accompany exposure to p-H_2, and to a thermal (290-K) D_2 gas. The behavior is similar to that of n-H_2, but the slopes are greater and saturation sets in earlier. In addition, the saturation value of $\Delta\phi$ for D_2 is greater than for H_2, reflecting the somewhat higher saturation density that results from the reduced zero-point motion of D_2. The enhancement is in rough correspondence with the surface densities of the bulk solids, 0.89 and 0.97×10^{15} mol/cm^2 for H_2 and D_2, respectively.[5]

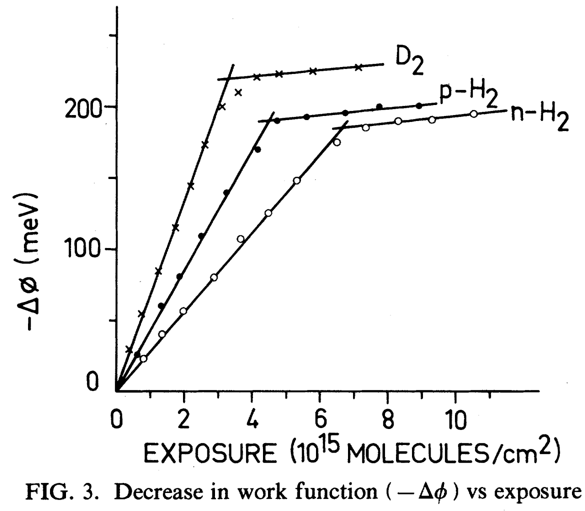

FIG. 3. Decrease in work function ($-\Delta\phi$) vs exposure for n-H_2 (○), p-H_2 (●), and D_2 (×) adsorbed on Cu(100) at 10 K (15 K for D_2).

Since the chemical compositions of H_2 and D_2 are essentially identical, and since the work-function change is a feature of the surface-potential well and so is only very weakly dependent on the rotational state of the adsorbed molecule, Fig. 3 allows a direct, accurate determination of the relative sticking coefficients. We find

$$\frac{S_{p\text{-}H_2}}{S_{n\text{-}H_2}}=1.5,\quad \frac{S_{D_2}}{S_{n\text{-}H_2}}=2.4\ . \tag{4}$$

Because the p-H_2, and n-H_2 gases are identical in all but their rotational populations, the former figure confirms the dependence of the sticking probability on the distribution of rotational levels in the incident gas.

III. STICKING VIA TRANSLATIONAL-ROTATIONAL CONVERSION

As mentioned in the Introduction, it is not easy to see how conventional sticking mechanisms, involving loss of normal energy ϵ_i^z to phonons or electron-hole pairs, can account for a strong dependence of the H_2-Cu(100) sticking coefficient on the rotational states of the gas-phase molecules. A mechanism involving translational-rotational conversion gives this dependence very naturally, however, as we now show. For simplicity, we will assume conservation of parallel momentum in all trapping events, though, as mentioned in Sec. IV, this may not correspond to the experimental conditions.

For a Maxwell-Boltzmann gas at temperature T_g, with relative rotational populations n_j, the fraction of molecules incident at the surface having normal kinetic energy in the range $\epsilon\rightarrow\epsilon+d\epsilon$, and in rotational state j, is

$$\rho_j(\epsilon)d\epsilon=\beta n_j e^{-\beta\epsilon}d\epsilon\ , \tag{5}$$

where $\beta=1/k_BT_g$. A molecule that excites rotationally from level j to level j', at the same time transferring to a bound level of the surface-potential well with energy $-\epsilon_m$ (<0), must have normal kinetic energy

$$\epsilon_{jj'}^m=\epsilon_{jj'}-\epsilon_m\ , \tag{6}$$

where

$$\epsilon_{jj'}=[j'(j'+1)-j(j+1)]B_{H_2}\ ,$$

with $B_{H_2}=7.35$ meV, the rotational constant for H_2. If we make allowance for the absorption of some energy $\Delta\epsilon_s$ by solid excitations and assume that $\Delta\epsilon_s$ is of the order of the interlevel spacings in the well,[9] then the molecules that can trap via rotational excitation $j\rightarrow j'$ lie in a band of normal kinetic energy between $\epsilon_{jj'}-\epsilon_0$ and $\epsilon_{jj'}$, where ϵ_0 is the well depth. The fraction of molecules in the entire gas that lies within one or other of these bands—i.e., the maximum possible trapping coefficient—is then given by

$$T=\sum_j n_j T_j,\quad T_j=(e^{\beta\epsilon_0}-1)\sum_{j'}{}' e^{-\beta\epsilon_{jj'}}\,, \tag{7}$$

where $\sum'$ implies a sum over even (odd) $j'>j$ according to whether j is even (odd). In deriving (6) we have assumed that $\epsilon_{jj'}>\epsilon_0$ for all relevant j and j' and that bands belonging to different j' do not overlap. This is valid for H_2, but not for D_2 or HD. The coefficient T_j gives the maximum coefficient for a gas composed entirely of molecules in rotational state j. Note that the *relative* values of the T_j depend neither on details of the well, nor on the assumption that ΔE_s is of the order of the level spacing, but only on the gas temperature T_g and rotational constant B. For $T_g=290$ K, and taking $\epsilon_0\sim 1/\beta\simeq 25$ meV, we find

$$T_j=0.30,0.09,0.03 \quad \text{for } j=0,1,2\,. \tag{8}$$

The fall off of T_j with increasing j simply reflects the increase in the energy of the lowest-lying attainable rotational excitation, i.e., $\epsilon_{jj+2}=(4j+6)B_{H_2}$ $=44,73,103$ meV for $j=0,1,2$. As j increases, the number of molecules in the gas that have sufficient normal energy to undergo the process of trapping via rotational conversion decreases sharply.

In order to use Eqs. (6) and (7) to calculate theoretical values for the sticking coefficient and population ratios determined experimentally [Eqs. (2)—(4)], we make the following assumptions concerning the sticking. (i) The actual trapping coefficients are proportional to their maximum values, with a j-independent proportionality constant. (ii) A fixed j-independent fraction of trapped molecules ultimately stick. These assumptions, which we discuss below, allow theoretical values for all *relative* quantities to be calculated directly from the gas-temperature T_g and the rotational constant B_{H_2}. That is, only ratios of the T_j enter, so that all details of the well and assumptions concerning the magnitude of the energy $\Delta\epsilon_s$ dissipated by solid excitations cancel out.

Specifically, the population ratio of particles trapped in rotational states $j=1,0$ is given by

$$\frac{P_1}{P_0}=\sum_{j_{\text{odd}}} n_j T_j \Big/ \sum_{j_{\text{even}}} n_j T_j\,, \tag{9}$$

where n_j are the gas-phase relative rotational populations. Similarly, the ratio of sticking coefficients for two H_2 gases characterized by relative spin populations n_j', n_j is

$$\frac{S'}{S}=\sum_j n_j' T_j \Big/ \sum_j n_j T_j\,. \tag{10}$$

We note that for H_2, all j sums are dominated by the first one or two terms. This is because of the large value of the rotational constant B_{H_2} and means physically that the H_2 trapped fraction needs to lose only one rotational quantum in order to stick permanently. If we apply the theory to D_2, we find that a non-negligible part of the trapped fraction is in the second rotationally excited state, while for HD, where the $\Delta j=2$ selection rule is relaxed, most of the "trapped fraction" is in states of rotational excitation higher than the first. As a second point, we remark that H_2 molecules counted as trapped have only this one possibility of changing their rotational quantum number. That is, the only quasielastic channel that is open besides the trapping channel is diffraction without change of rotational state. For D_2, a small fraction of the particles could scatter with gain or loss of a rotational quantum, while for HD, most of the particles that could trap, could also scatter into several other quasielastic channels. For this reason, the assumptions (i) and (ii) above are more plausible for H_2 than for D_2, and are not at all plausible for HD.

We postpone further discussions of the details of the adsorption process and now compare the predictions of (9) and (10) with the experimentally determined ratios given in Sec. II. Consider first the population ratio P_1/P_0 for n-H_2, whose rotational distribution is accurately known. Applying (9) we find a value of 1.4, very close to the experimental estimate of 1.3 [see Eq. (2)]. Consider next the ratio of sticking coefficients $S_{p\text{-}H_2}/S_{n\text{-}H_2}$. To apply (10) we need to know the spin populations of the incident gas p-H_2. If this were pure para, we would have $n_j=0.53,0.0,0.46$ for $j=0,1,2$ and (10) then gives a value of 1.7, compared with the experimental value of 1.5 [see Eq. (4)]. However, as Fig. 1 makes clear and as was mentioned in Sec. II, the incident p-H_2 gas was not pure para, and if we assume an ortho-para ratio of 0.25, giving spin populations $n_j=0.42,0.18,0.36$, Eq. (10) reproduces the observed figure for $S_{p\text{-}H_2}/S_{n\text{-}H_2}$ of 1.5. Taking these values for the spin populations, we use (9) without further assumption to determine a theoretical population ratio P_1/P_0 for p-H_2, obtaining 0.12 in reasonable agreement with the experimental estimate of 0.2 [see Eq. (3)]. As a final application we use (10) to calculate the sticking coefficient ratio $S_{n\text{-}D_2}/S_{n\text{-}H_2}$, taking the appropriate n_j and T_j for n-D_2 (ortho-para ratio 2, $B_{D_2}=3.71$ meV). We find $S_{n\text{-}D_2}/S_{n\text{-}H_2}=3.1$, compared with the accurate measured value of 2.4 [Eq. (4)]. While this is something of an overestimate, a too large value is consistent with the above discussion concerning the relative availability of quasielastic channels for D_2 and H_2. We conclude that the observed population and sticking coefficient ratios are consistent with the rotational excitation mechanism for the sticking.

IV. DISCUSSION AND SUMMARY

The EELS and work-function measurements during adsorption of H_2 from the gas phase on a cold Cu(100) crystal surface demonstrate conclusively that the sticking coefficient depends on the relative rotational populations in the gas. This conclusion is independent of any theoretical interpretation. The conventional view of sticking assumes an initial trapping step involving dissipation of the gas-phase normal kinetic energy by phonons or electron-hole pairs. For this to be compatible with the measurements, the coupling to solid excitations would have to depend strongly on the rotational state of the incoming molecule. Though such a dependence cannot be ruled out, it seems unlikely that it could be strong enough to reproduce the measured sticking coefficient ratio. If trapping occurs via simultaneous excitation of the solid and rotational excitation of the molecule, however, the effect observed is easy to understand because the number of molecules in a Maxwell-Boltzmann gas that can trap depends on the relative populations of the rotational levels. Assuming that the sticking coefficient is proportional to this number, we have shown that the measured sticking coefficient ratios for two H_2 gases and for H_2 and D_2 gases, as well as the relative populations of ortho- and para-H_2 physisorbed on the surface, can be understood semiquantitatively.

Although we believe this is a substantial piece of evidence in favor of the proposed mechanism, there are some observations that are not easy to interpret. First, whereas the theoretical sticking coefficient ratio for thermal mixtures of HD and H_2 is ~ 7, the relative slopes of the work function versus exposure curves give a value of 2.0. That is, the observed sticking coefficients for HD and D_2 are rather similar. This would seem at first sight to contradict the rotational-conversion mechanism in that the coupling of center of mass and relative motion is expected to be far stronger for HD than for H_2 or D_2 because of the asymmetry of the molecule with respect to its center of mass. In fact, scattering experiments on Pt showed almost complete rotational conversion of HD molecular beams.[10] One explanation for the rather low sticking coefficient of HD was mentioned in Sec. III. Most of the HD molecules in a thermal distribution that can trap can also scatter back into the gas phase with change of rotational quantum number. As the beam experiments show, the cross section for this competitive scattering is large. For H_2, by contrast, such channels are closed to molecules that can trap. This is because of the $\Delta j = 2$ selection rule and the relatively larger value of the rotational constant.

A second interpretative difficulty concerns the absolute value of the sticking coefficient. Both the EELS spectra for physisorbed H_2 (Ref. 2) and the data for the scattering of a 77-meV H_2 molecular beam from a 70-K Cu(100) surface[11] imply a weak coupling of rotational and center-of-mass motion. This is also consistent with a recent calculation of the interaction.[3] Accordingly, we would expect to find a rather low cross section for trapping via rotational conversion and hence a low absolute sticking coefficient. A precise experimental determination of this quantity from the available kinetic data would require knowledge either of the electric dipole induced by a physisorbed molecule, or the saturation density of physisorbed molecules on the surface. Neither quantity is easily measurable. However, we might expect the saturation density to be roughly the same as for solid H_2, $\bar{n} \sim 10^{15}$ mol/cm^2. This value, which is consistent with the absolute intensity of the EELS lines,[2] corresponds to $S_{n\text{-}H_2} \sim 0.15$. According to the discussion of Sec. III, however, the maximum possible value of $S_{n\text{-}H_2}$, equal to the fraction of gas-phase molecules that have normal energy within the range that would allow the process to take place, is 0.1. The experimental estimate therefore seems to be consistent with the rotational-conversion mechanism only if every particle that can undergo the process does so, implying a very strong coupling between center of mass and relative motion, for which there is no direct evidence.

This inconsistency may be due to the assumption we made concerning conservation of parallel momentum in trapping events. A consequence of this assumption is that, for example, $j = 0$ H_2 particles with normal energy less than ~ 20 meV—i.e., $\sim 60\%$ of all incident particles—cannot trap. Many of these, however, approach the surface at large angles of incidence for which scattering events involving collisions with surface imperfections or impurity atoms are relatively probable. Such particles can trap by translational-rotational conversion provided their *total* incident kinetic energy exceeds $\epsilon_{jj'} - \epsilon_0$. The sticking coefficient is then proportional to the fraction of incident particles having a large angle of incidence and sufficient total kinetic energy to excite the lowest available rotational excitation. Since this fraction is determined primarily by Boltzmann factors $\sim \exp[-\beta(\epsilon_{jj'} - \epsilon_0)]$, the relative sticking coefficients for gases with differing rotational populations would be very similar to the ideal surface values used in the comparison with experiment. On this basis one can reconcile the large value of the absolute sticking coefficient with the observed dependence on rotational populations.

In summary, by monitoring EELS intensities of rotational transitions and the change in work function as an H_2 gas physisorbs on a cold Cu(100) surface, we have demonstrated that the sticking coefficient depends on the populations of rotational levels in the gas. The observed variation of the sticking coefficient is compatible with a sticking process whereby most of the molecules' center-of-mass kinetic energy is converted on impact into rotational energy. Only a small fraction of this energy needs to be dissipated by phonon processes during the collision. The H_2-Cu(100) system is very favorable for investigation because of the large spin energies involved, the absence of coupling between ortho- and para-species, and the free-molecular nature of the rotation spectrum. It is likely, however, that translational-rotational conversion plays an important role in the sticking of most molecules on most surfaces.

ACKNOWLEDGMENTS

We thank M. Pettersson and E. Törnqvist for valuable assistance during the preparation and analysis of the para-H_2 gas. This work was supported financially by the Swedish Natural Science Research Council (S.A.) and by the Nordic Institute for Theoretical Atom Physics (NORDITA) (J.H.).

---

[1] This view was first emphasized by R. Zwanzig, J. Chem. Phys. 32, 1173 (1960). For more recent work, see, e.g., R. Sedlmeir and W. Brenig, Z. Phys. B 36, 245 (1980); R. Brako and D. M. Newns, Solid State Commun. 33, 713 (1980); J. W. Gadzuk and H. Metiu, Phys. Rev. B 22, 2603 (1980); K. Schönhammer and O. Gunnarsson, *ibid.* 22, 1629 (1980).

[2] S. Andersson and J. Harris, Phys. Rev. Lett. 48, 545 (1982).

[3] J. Harris and A. Liebsch, Proceedings of the First Nordic Conference on Surface Science [Phys. Scr. (in press)].

[4] S. Andersson, C. Nyberg, and C. G. Tengståhl (unpublished).

[5] See, e.g., I. F. Silvera, Rev. Mod. Phys. 52, 393 (1980).

[6] E. S. Chang and A. Temkin, Phys. Rev. Lett. 23, 399 (1969).

[7] The hydrogen pressure read by the ionization gauge was multiplied by a correction factor of 3.5. This value was estimated from an indirect comparison with a calibrated gauge.

[8] A decrease is expected on two counts; (a) the van der Waals dipole polarizes the H_2 $1\sigma_g$ orbital slightly towards the metal, and (b) the Bloch electrons are expelled from the region close to the molecule and returned to the metal.

[9] The calculation of Ref. 3 gave a level sequence 19,11,6,2.8,1.2,0.4 meV for H_2, which is in surprisingly good correspondence with recent measurements of the selective adsorption spectra [J. Lapujoulade (private communication)].

[10] J. P. Cowin, Chien-Fan Yu, S. J. Sibener, and J. E. Just, J. Chem. Phys. 75, 1033 (1981).

[11] J. Lapujoulade, Y. Le Cruer, M. Lefort, Y. Lejay, and E. Maurel, Surf. Sci. 103, L85 (1981).