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## Scattering of swift, neutral molecular hydrogen from Ni(110)

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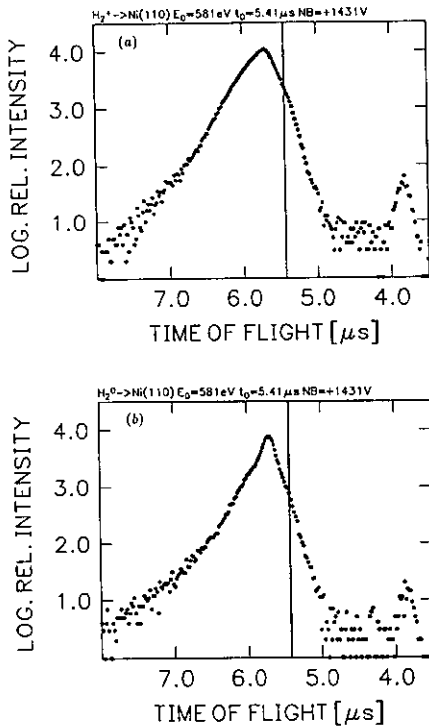
**Abstract.** The scattering of hydrogen from metal surfaces is of interest in nuclear fusion research for two reasons: (i) the plasma–wall interaction and (ii) the production of intense neutral hydrogen beams for refuelling and heating. The Ni–H system is also of basic interest in surface chemistry and physics for reasons of hydrogen storage, catalysis and fuel cells. Studies of hydrogen interaction with surfaces are proceeding and a discussion follows as to the mechanism of dissociation of the incident molecules.

The scattering of hydrogen from metal surfaces is of interest in nuclear fusion research for two reasons, (i) the plasma–wall interaction and (ii) the production of intense neutral hydrogen beams for refuelling and heating. Undoubtedly hydrogen interaction with surfaces is also a basic subject of surface physics and chemistry. After first studies of the interaction of swift (5 keV) hydrogen molecules (Eckstein *et al* 1975) with a Au surface (polycrystal), it was the detection of negative, molecular oxygen scattered from Ag that demonstrated the correlation of this type of experiment with surface chemistry (Pan Haochang *et al* 1986). Since then a number of other molecules have shown the effect of harpooning, i.e. the capture of electrons, in qualitative agreement with surface chemistry experiments and theory (Heiland 1991). The basic physics of the interaction process is under discussion. Essentially all experiments show, in addition to the survival of molecules, the dissociation of the incident molecules. There are at least two different processes possible for the dissociation. The molecule, especially if it is a positive ion, may dissociate by charge capture. In the case of  $H_2^+$ , capture can occur into the *ungerade*, antibonding triplet state. On the other hand, the molecule may dissociate by a rovibrational excitation. In the case of negative-ion formation, the dissociation may proceed from that state, or may be enhanced by additional rovibrational excitation.

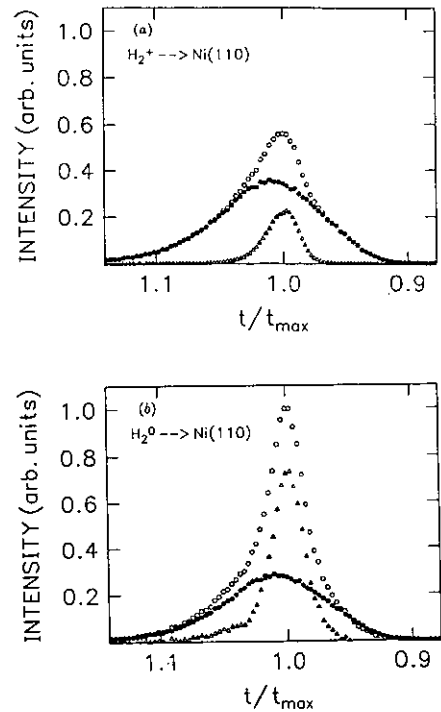
Hydrogen has no stable  $H_2^-$  state, so this excitation plays no role in the interaction process. Measurements of the dissociation of fast  $H_2^+$ ,  $N_2^+$ ,  $CO^+$ ,  $CO_2^+$  and  $O_2^+$  at K-covered Ni surfaces show that the negative molecular states play a major role in the dissociation only in the case of  $CO_2$  and  $O_2$  (Schubert *et al* 1990, Heiland 1991). Neutralization is however a dominant event: ion yields of the scattering of  $H_2^+$  at grazing incidence from Ni (Willerding *et al* 1984a) and Ag (van Slooten *et al* 1991, 1992) are below 1%. The other results from these two groups are not directly comparable for a number of reasons: different surfaces and different angles of incidence are used. The experiments of van Slooten *et al* (1992) include data from neutral  $H_2$  incident on silver; however, only the scattered ions,  $H_2^+$  and  $H^+$ , are

analysed. Here we report results from the scattering of  $H_2$  from Ni(110) where both scattered ions and neutrals are analysed.

The experimental arrangement has been described in detail (Willerding *et al* 1984b). It is an ultra-high-vacuum (UHV) system providing a pulsed, magnetically analysed ion beam, target handling and time-of-flight analysis (TOF) of the scattered particles. We added a gas cell between magnet and target for producing neutral beams (Schmidt 1992).



**Figure 1.** Time-of-flight spectra of  $H_2^+$  and  $H_2^0$  incident on Ni(110) at grazing incidence ( $\psi = 5^\circ$ ) and a primary energy of 581 eV. Negative ions ( $H^-$ ) appear at shorter flight times (3.9  $\mu$ s) due to postacceleration. The intensity scale is logarithmic. The neutral peak at 5.7  $\mu$ s contains dissociated atoms and surviving molecules. The perpendicular line marks  $t_0$ .



**Figure 2.** The same data as in figure 1,  $H_2^+$  and  $H_2^0$  incident on Ni(110) with a linear intensity scale. The spectra are separated into H and  $H_2$  components. ● show the experimental data, ○ are the estimated H atoms and Δ the surviving  $H_2$  molecules.

Results for beams of about 600 eV  $H_2^+$  and  $H_2^0$  are shown in figures 1 and 2. These are TOF spectra, where the abscissa runs from right to left, i.e. it is essentially an energy scale running from left to right. The ion peaks are separated from the neutrals by postacceleration. In figure 1 we use a logarithmic intensity scale, in figure 2 the scale is linear. Since at 600 eV the sensitivity of the channel-plate of the TOF detector is of the same order of magnitude for ions and neutrals, we estimate the ion yields  $H^-/(H^0 + H_2^0 + H^-)$  to be of the order of  $10^{-2}$  to  $10^{-3}$ . The positive-ion yields (not shown here) appear to be somewhat lower, indicating a small reionization probability. From this finding we conclude also that there is a small survival probability for ions

in the case of  $H_2^+$  as the primary particle. Since we focused our attention on the neutral part, the experiments were performed such that we have good statistics in the neutral peak. In the neutral peak we find an increase in the small molecular peak riding on top of the broad hump of dissociated particles (figure 2). In the linear representation of figure 2 the atomic peaks of incident  $H_2^+$  and  $H_2^0$  are fitted to the same relative intensity for the high-energy part of the spectra. From the dissociation, the atoms have an additional kinetic energy given by

$$E = \frac{1}{2}E_0 + \frac{1}{2}E_D \pm \sqrt{E_0 E_D} \cos \alpha$$

where  $E_0$  is the primary energy,  $E_D$  the dissociation energy and  $\alpha$  the angle of the molecular axis to the beam direction. Therefore, particles with energies above  $E_0$  have to be dissociated particles. The equality of the two spectra of dissociated H atoms suggests that the neutralization and dissociation are fast processes, i.e. 'memory' of the initial charge state is destroyed.

Based on previous results for H-Al of Imke *et al* (1987) we estimate the shape of the spectra of the dissociated particles (figure 2). We then can evaluate the molecular survival ratio  $H_2^0/(\frac{1}{2}H + H_2^0)$  for the two cases. We find 0.20 for incident  $H_2^+$  and 0.36 for incident  $H_2^0$ , i.e. the yield of  $H_2$  from  $H_2^0$  is about a factor of two higher than for  $H_2^+$ . The accuracy of the survival yields is  $\pm 0.05$ .

The straightforward interpretation of the result is that with  $H_2^+$  neutralization occurs partly into the  $b^3\Sigma_u$  state which leads to dissociation. With  $H_2^0$  this process can occur only after the molecule has been ionized; however, this process is very unlikely. This finding agrees with previous conclusions (Willerdig *et al* 1984a, van Slooten *et al* 1992, Tappe *et al* 1990). Nevertheless the molecular survival probability of  $H_2^0$  is small compared to that of  $N_2^+$ , which is 0.95 under comparable conditions (Schubert *et al* 1990). The question remains of which process causes the dissociation of  $H_2^0$ . It could be rovibrational excitation and/or the dynamical screening of the hydrogen penetrating into the electron selvage of the surface (Flores 1991). Within a solid, slowly moving ( $v \ll v_0 = 2.2 \times 10^8$  cm s<sup>-1</sup>) hydrogen atoms are screened dynamically by two electrons, so a molecular bond is not possible. The screening action is governed by the dielectric response function of the solid. As argued before (Närmann *et al* 1991), the 'effective' surface for the bulk dielectric response function is positioned at a distance  $D = x_0 + \frac{1}{2}s$  above the last atomic layer, where  $s$  is the interplanar spacing (for Ni,  $s = 2.55$  au) and  $x_0$  is the centre of mass of the induced charge-density distribution (for  $r_s = 2$  we have  $x_0 = 1.6$  au) (Lang 1973). Since for Ni the one-electron density  $r_s < 2$ , we obtain  $D = 1.52$  Å as a lower limit. Trajectory calculations show that hydrogen atoms scattered at angles of incidence of  $5^\circ$  at 600 eV are channelled along the surface (Höfner *et al* 1992). This behaviour does not change when we simulate  $H_2$  by a particle with mass  $m = 2$  and atomic number  $Z = 2$ , i.e. we assume  $H_2^0$  to be spherical. The particles do not penetrate into the solid, but are scattered at about 1 Å above the first layer of Ni ion cores. Trajectory lengths are between 10 and 15 Å if we assume that the electronic interaction with the surface electrons becomes important at  $d = 1.3$  Å above the Ni ion cores (Närmann *et al* 1990). That is, there are no violent collisions and the penetration into the electron cloud is rather shallow, but well within the Lang limit of  $D = 1.52$  Å. Violent collisions with defects (steps) are unlikely, since we use the same Ni(110) crystal as for the previous  $N_2^+$  measurements (Schubert *et al* 1990, Heiland 1991), where we found no evidence for violent collisions, even on a surface partly covered with K. If

we assume the characteristic time for the screening to be of the order of  $10^{-15}$  s, the mean free path will be (at a velocity of  $3 \times 10^7$  cm s $^{-1}$ ) of the order of 3 Å. The trajectory lengths are about three to five times the mean free path, i.e. dissociation is quite possible. Recently the dissociation of H<sub>2</sub> on Rh(001) was treated theoretically on the basis of first-principles local-density-functional theory (Feibelman 1991). It is found that 'thermal' hydrogen dissociates at  $2.98a_0$ , or 1.5 Å above the Rh ion cores. For the trajectory length estimate we use a limit of 1.3 Å above the Ni ion cores, close enough to the theoretical value for a first estimate.

However, a direct comparison of our results with thermal hydrogen experiments and with corresponding theories may pose major problems simply due to the speed of the particles and due to the larger penetration depth reached. Any dissociative 'seam' of a potential-energy surface (PES) is crossed fast in our experiment, so the application of PES models may be questionable. On the other hand the screening of fast H in a metal is based on a well established theory for the velocities in question here (Flores 1991). However, a detailed calculation for impinging H<sub>2</sub> and a comparison with 'static' theories has yet to be done.

In summary, we propose, on the basis of the experimental evidence presented, that H<sub>2</sub><sup>0</sup> is, to a sizeable extent, dissociated by electronic interactions. If the incoming particle is H<sub>2</sub><sup>+</sup>, a large fraction is dissociated by resonant electron capture into the  $b^3\Sigma_u$  state. The remaining molecules are neutralized into the ground state. They either survive or are dissociated by dynamical screening.

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### References

- Eckstein W, Verbeek H and Datz S 1975 *Appl. Phys. Lett.* **27** 527  
Feibelman P J 1991 *Phys. Rev. Lett.* **67** 461  
Flores F 1991 *Interaction of Charged Particles with Solids and Surfaces* ed A Gras-Marti, H M Vrbansek, N R Arista and F Flores (New York: Plenum)  
Heiland W 1991 *Fundamental Aspects of Heterogenous Catalysis Studied by Particle Beams* ed H H Brongersma and R A van Santen (New York: Plenum)  
Höfner C, Närmann A and Heiland W 1992 *Nucl. Instrum. Methods B* at press  
Imke U, Schubert S, Snowdon K J and Heiland W 1987 *Surf. Sci.* **189/190** 960  
Lang ND 1973 *Solid State Physics* vol 28 (New York: Academic) pp 225  
Närmann A, Heiland W, Monreal R, Flores F and Echenique PM 1991 *Phys. Rev. B* **44** 2003  
Närmann A, Monreal R, Echenique PM, Flores F, Heiland W and Schubert S 1990 *Phys. Rev. Lett.* **64** 1601  
Pan Haochang, Horn T C M and Kleyn A W 1986 *Phys. Rev. Lett.* **57** 3035  
Schmidt K 1992 *Thesis* University of Osnabrück, unpublished  
Schubert S, Imke U and Heiland W 1990 *Vacuum* **41** 252  
Tappe W, Niehof A, Schmidt K and Heiland W 1991 *Europhys. Lett.* **15** 406  
van Slooten U, Andersson D, Kleyn A W and Gislason E A 1991 *Chem. Phys. Lett.* **185** 440  
— 1992 *Surf. Sci.* **274** 1  
Willerding B, Heiland W and Snowdon K J 1984a *Phys. Rev. Lett.* **53** 2031  
Willerding B, Steininger H, Snowdon K J and Heiland W 1986b *Nucl. Instrum. Methods B* **2** 453