

CHEMISORPTION OF ATOMIC HYDROGEN ON CLEAN AND Cl-COVERED Ag(111)

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The chemisorption of atomic hydrogen and deuterium on clean and Cl-covered Ag(111) has been studied using temperature programmed desorption (TPD), work function change ($\Delta\phi$) measurements and ultra-violet photoelectron spectroscopy (UPS). The desorption of molecular hydrogen and deuterium follows a fractional-order kinetic description with an activation energy of 5.5 kcal/mol (H_2) and 6.4 kcal/mol (D_2). Based on these results and the absence of dissociative chemisorption at 100 K, an upper limit for the Ag–D(H) bond of 53. (52) kcal mol⁻¹ is derived. UPS reveals an H(1s)-derived bonding state at about 7.3 eV below the Fermi level. There are no significant changes in the shape of the Ag d-band, consistent with its, at most, very weak involvement in the D–Ag bond. Saturation exposure of the clean Ag(111) surface to atomic D results in a $\Delta\phi$ of -0.17 eV. Surface Cl alters the bonding and reduces the saturation coverage of D, results that are interpreted in terms of each Cl controlling a large number of D(a) adsorption sites and leading to widely varying local surface coverages.

1. Introduction

The interaction of hydrogen with metal surfaces is of fundamental interest to surface scientists and has been reviewed recently by Christmann [1]. However, the interaction of hydrogen atoms with Ag surfaces has received little attention [2] because, like Cu and Au, there is a large activation barrier for the dissociative chemisorption of H_2 . This barrier separates the shallow molecular physisorption well from the atomic chemisorption site [3,4]. It appears to be due to the absence of unoccupied d states [5] near the Fermi level of these metals. This pattern is followed for many metals having no empty d states near the Fermi energy, for example, Cu(111), Cu(110) and Cu(100) [6,7], Au films [8], Zn(0001) [9], Al(111) and Al(100), and Na and K

films [10,11]. Exceptions are high index Cu(211), Cu(311) and Cu(755) surfaces and polycrystalline Cu films on which dissociative adsorption of hydrogen has been claimed [7].

While the chemical behavior of atomic hydrogen on Ag(111) has not, to our knowledge, been reported, it is an important issue for our understanding of Ag as a catalyst, with and without added Cl, for reactions that involve hydrogen and for our understanding of how Ag compares to other Group IB metals. Toward an understanding of this surface chemistry, we report here on the chemisorption of *atomic* deuterium and hydrogen on clean and Cl-covered Ag(111) surfaces. We limit ourselves to a survey of the adsorption/desorption behavior of atomic hydrogen and deuterium and have not undertaken to answer detailed surface physics questions concerning surface relaxation/restructuring and surface electronic bandstructure. Rather, our focus is on obtaining data that is of central importance for characterizing surface reaction kinetics. Atomic hydrogen, produced by a hot W-filament [6,9–13], is readily adsorbed at 100 K, desorbs with two peaks, both below 200 K, lowers the work function of Ag(111), and exhibits a valence band photoemission spectrum typical of atomic hydrogen on other metals. As expected, we found no evidence for the dissociative adsorption of hydrogen on Ag(111) for exposures up to 10^4 L.

2. Experimental

The experiments were performed in an ion-pumped UHV chamber which has been described in detail previously [14]. Briefly, the chamber was equipped with a Perkin-Elmer double-pass CMA with coaxial electron gun, a helium discharge lamp, a sputtering gun and a UTI 100C quadrupole mass spectrometer (QMS). The chamber had an auxiliary 170 ℓ /s turbomolecular pump and a titanium sublimation pump. The base pressure was typically 5×10^{-10} Torr.

The mounting and cleaning procedure of the Ag(111) crystal has been reported previously [15]. The sample was cooled to ~ 100 K with liquid nitrogen. The temperature was measured with a chromel–alumel thermocouple spot-welded to a Ta loop that was pressed into a hole drilled in the edge of the Ag crystal. For TPD, a temperature ramp of 4 K/s was generated by a home-made controller. UPS was done using a 25 eV pass energy on the CMA. $\Delta\phi$ was determined from the low kinetic energy threshold of secondary emission of the He I UPS spectra.

The atomic D and H were produced by decomposition of H_2 and D_2 on the filament of the mass spectrometer. The exposures were made with the sample (at ~ 100 K) facing the filament and by backfilling the chamber with D_2 or H_2 at 5×10^{-6} Torr. Saturation exposure was obtained in about 30 min. Due to the unknown dissociation efficiency of D_2 (H_2) and the unknown absolute

D coverage, the coverages of D (H) reported below are normalized to saturation on clean Ag(111), $\sigma \equiv 1$.

Surface Cl was prepared by first decomposing chemisorbed CH_3Cl by exposure to electrons from the filament of the QMS and then flashing the surface to 600 K to desorb undecomposed CH_3Cl and C_1 fragments. All the C_1 fragments desorb as C_xH_y hydrocarbon products, leaving only Cl on the surface [16].

3. Results and discussion

3.1. Molecular hydrogen and deuterium TPD with and without coadsorbed Cl

At the outset, we note that, as expected, doses of 10^4 Langmuir units (L) of D_2 produced no measurable uptake of D(a). Turning to atomic D uptake, we see in fig. 1 the TPD spectra of D_2 and H_2 from clean and Cl-covered Ag(111). The coverages, normalized to saturation, of atomic species were prepared with the substrate at ~ 100 K. At low coverages on the clean surface, D_2 desorbs as a single peak. At saturation coverage, $\sigma_{\text{D}} = 1$ in fig. 1, D_2 desorbs with a peak at 198 K and a shoulder at lower temperature, 173 K. The shoulder contains about 25% of total D_2 desorbed. Compared to D_2 , desorption of H_2 follows the same trends but with slightly lower peak temperatures. As shown in fig. 1, both the onset and the peak temperature are about 7 K lower for H_2 than for D_2 . This indicates that there is a small isotope effect in desorption on Ag(111), favoring H.

Surprisingly, the desorption of D_2 does not follow simple second-order atomic recombination kinetics as commonly observed on most transition metal surfaces and as observed on Ni(100) using this instrumentation [14]. In fig. 1, the peak temperature shifts higher as the D coverage increases, suggesting zero-order kinetics, but the leading edges are not superimposable, indicating non-zero-order kinetics. Apparently, the desorption of D_2 on Ag(111) obeys a fractional order kinetics as found on Zn(0001) [9].

Fractional order desorption kinetics is consistent with island formation, which could arise due to attractive interactions between neighboring chemisorbed D or H atoms. Attractive lateral interactions and small barriers to lateral diffusion of atomic hydrogen are not unreasonable for this system, given the propensity for forming H_2 (D_2) at such low temperatures. Other possibilities for the unusual behavior of the TPD peaks – shifts to higher temperature, low-coverage curves crossing higher-coverage curves, and the development of a new higher temperature peak as the coverage increases – include subsurface hydrogen and non-equilibrium effects. Using high energy H^+ , formed in the Ar^+ sputter cleaning source [26], we can rule out a major role for H deep within the subsurface region. This does not eliminate a coverage-dependent

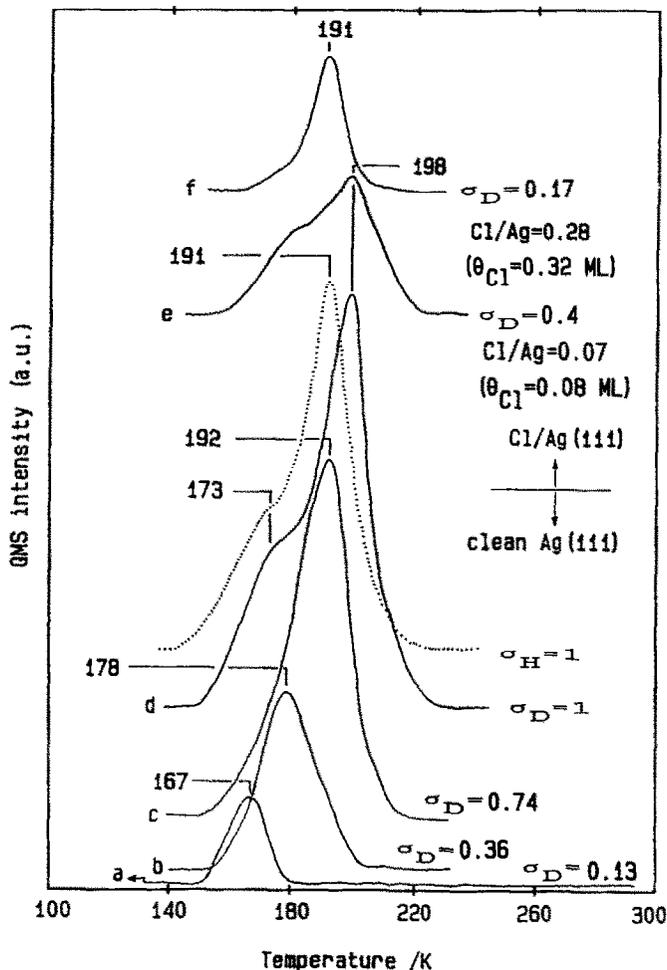


Fig. 1. TPD spectra of D_2 and H_2 on clean and Cl covered Ag(111). The coverages are normalized to saturation on the clean surface, $\sigma = 1$. The dotted curve is H_2 TPD after a saturation exposure (30 min) of atomic H on the clean surface. For the Cl-covered surfaces, the relative amount of Cl is expressed as Cl(181)/Ag(256) AES ratio. The estimated values of θ_{Cl} in ML based on Bowker and Waugh's calibration [18] of θ_{Cl} versus Cl/Ag AES ratio are shown in parentheses. The exposures were made at ~ 100 K. The temperature ramp rate was 4 K/s.

distribution of atomic H lying above and below the first layer of Ag atoms. However, see discussion in section 3.4. Strong non-equilibrium effects are ruled out on the basis of varying the TPD ramp speed. While the TPD spectra of fig. 1 obviously do not fit a simple kinetic description, we proceed here with an empirical description in terms of fractional order kinetics. To get an

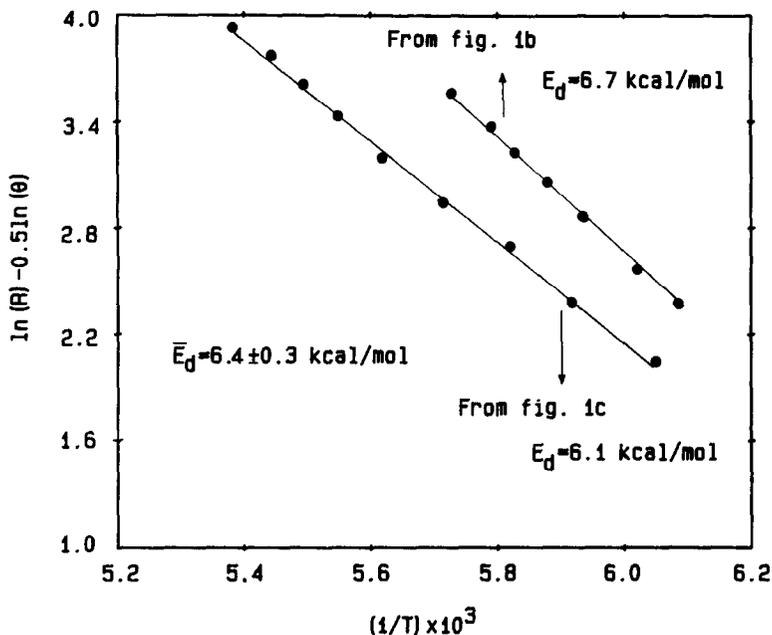


Fig. 2. Half-order plots of $\ln(R) - 0.5 \ln(\theta)$ against $1/T$ (corresponding to figs. 1b and 1c). R is the instantaneous relative TPD intensity at T and θ is the coverage remaining on the surface. The latter is proportional to the TPD area above T .

approximation for the effective activation energy, the results are analyzed using the following equation [17]:

$$R = -d\theta/dT = (\nu/\beta)\theta^n \exp(-E_d/RT), \quad (1)$$

where ν is the pre-exponential factor, β the heating rate, n the reaction order, and E_d the desorption activation energy. Assuming ν and β are constant and that $n = 0.5$, plotting $\ln(R) - 0.5 \ln(\theta)$ against $1/T$ yields E_d from the slope, R , θ and T can be readily obtained from the TPD curves. Using the leading edges of fig. 1b and 1c (i.e., considering only the kinetics of the early stages of desorption), the linear plots shown in fig. 2 are obtained. Thus, the assumption of half-order kinetics is reasonable. The plot from fig. 1b yields $E_d = 6.7$ kcal/mol and that from fig. 1c yields $E_d = 6.1$ kcal/mol, so we conclude that in this intermediate coverage range, the early stages of desorption are adequately described by half-order kinetics with an effective average activation energy of 6.4 ± 0.3 kcal/mol. Determination of ν is not possible since absolute values of R are unknown. A similar analysis of data for H_2 TPD (not shown) gives $E_d = 5.5 \pm 0.3$ kcal/mol.

Turning our attention to Cl-covered surfaces, we find that when Cl is preadsorbed and a saturation dose of D is given, the characteristics of the

TPD change. No DCl is found in TPD, and Cl desorbs as AgCl above 700 K. At low Cl coverages, $\theta_{\text{Cl}} = 0.07$ ML [18] (fig. 1e), the D_2 peak shape and peak position are indistinguishable from that found in the absence of Cl, fig. 1d, but the saturation coverage is reduced by 60%. This suggests that small amounts of Cl control relatively large regions of the Ag surface, making them unavailable for adsorption of D atoms. The remainder of the surface is not influenced strongly so that the *local* coverage of D at saturation is the same in these unperturbed regions as in the absence of Cl. As the coverage of Cl is increased, $\theta_{\text{Cl}} = 0.28$ (fig. 1f), the saturation coverage of D drops even further and the peak shape and position change; the main peak temperature drops and the low temperature shoulder is much weaker. We suppose that at these coverages, sites that acquire D are all influenced by Cl and probably lie at the boundaries between ordered islands of adsorbed Cl. According to this model, the local surface concentration of D is very inhomogeneous in the presence of Cl. Keeping in mind these differences in local coverage, we can only conclude that the same *average* coverage of D on 0.32 ML of Cl/Ag(111) is more stable than on clean Ag(111) (compare figs. 1a and 1f). In this sense, Cl stabilizes D. We note parenthetically that at high coverages of Cl and long doses of atomic D, there is some loss of Cl AES signal during the dose ($\leq 15\%$ over 30 min), which we attribute to electron-stimulated desorption of Cl^- and/or DCl. This weak effect does not alter the main conclusions drawn here.

For comparison, on Ni(100), Kiskinova and Goodman [19] report that surface Cl reduces the saturation coverage of H so strongly that when $\theta_{\text{Cl}} > 0.2$ ML, there was no dissociative chemisorption of H_2 [19]. In the absence of Cl, Ni(100), unlike Ag(111), displays second order H_2 desorption kinetics. These experiments are, of course, qualitatively different from what we report here; the dissociation of molecular hydrogen at the surface plays no role in our experiments. We suspect that exposure of atomic hydrogen to Cl/Ni(100) would lead to significant adsorption even for 0.2 ML of Cl. One other point concerning the Ni(100) results should be made. The presence of Cl destabilizes H(a) to some extent.

3.2. Work function changes

On clean Ag(111), the work function does not change upon exposure to D_2 , confirming the absence of dissociative chemisorption. The work function decreases by 0.17 eV ($\Delta\phi = -0.17$ eV) upon saturation by exposure to atomic D. That the work function changes confirms adsorption on Ag(111). The negative work function change indicates that the dipole character (amount of charge separated x distance separated) of the surface covered with D is less negative (towards the vacuum) than for the clean surface. Since, as noted earlier, we do not know the position of the D atoms with respect to the plane of the surface Ag atoms, this change cannot be interpreted microscopically.

3.3. UPS of D/Ag(111)

Fig. 3 shows the HeII UPS spectra of clean (dashed curve) and D-saturated (solid curve) Ag(111). The dashed curve was unchanged by exposure to D₂. On the D-covered surface, the Ag d-band is clearly attenuated, indicating significant electron scattering due to adsorbed D. After taking the difference between solid and dashed curve (lowest curve), a peak at about 7.3 eV is evident and, though small, is reproducible. In other UPS studies of hydrogen chemisorption on metal surfaces, similar data has been obtained and treated in the same way. There is typically a weak H-induced peak in this binding energy region: 6.2 eV on Cu(111) [6], 5.8 eV on Ni(111), 6.4 eV on Pd(111) and 7.3 eV on Pt(111) [20], 5.7 eV on W(100) and 6.3 eV on W(110) [21] and 7.2 eV on Ni(100) [14]. Therefore, we attribute the broad peak at 7.3 eV to the chemisorption bond between D(a) and Ag(111) [6,20]. This bond involves both the D(1s) orbitals and the band structure of the substrate; the intensity is, therefore, spread over a broad energy regime.

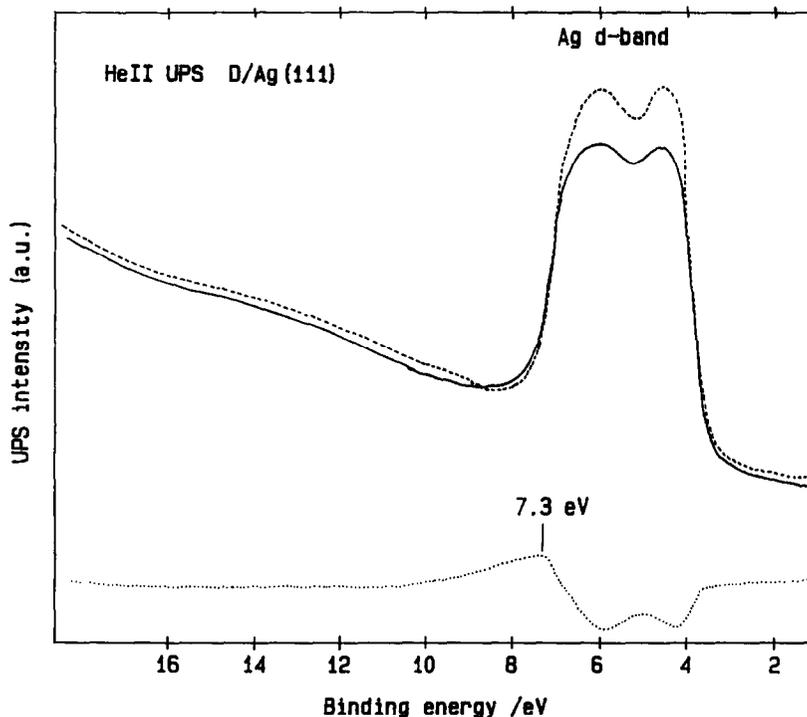


Fig. 3. HeII UPS spectra. The dashed curve is for the clean surface. The solid curve is for the surface with $\sigma_D = 1$. The bottom dotted curve is the difference between the solid and the dashed curve. The spectra were taken at ~ 100 K.

3.4. Desorption and bonding compared to other metals

The chemisorption of H on transition metal surfaces typically alters their d-band structures significantly. For example, chemisorbed H induces a nearly uniform d-band *enhancement* on Ni(111) and a strong *redistribution* of d-band emission on Pd(111) and Pt(111) [20]. These changes in the d-band structures are probably associated with bonding interactions with H although theoretical studies [22–24] argue that H adsorption on metals occurs primarily through interaction of the H(1s) orbital with the metal sp band rather than the metal d band. Since we observe no change in shape of the Ag d-bands, we suppose that there is, at most, a very weak interaction between the H(1s) and Ag(d) states. By comparison, Cu(111) is very different in that quite dramatic charge redistributions within its d-bands are induced by H [6].

The differences between Cu(111) and Ag(111) extend to thermal desorption of H₂. In the first place, on Cu(111) [6], the recombinative desorption of atomic H obeys second-order kinetics, unlike the fractional order kinetics observed here. In the second place, H(a) is bound much more tightly on Cu(111) than on Ag(111). While the H₂ TPD peak *shapes* from Ag(111) and Cu(111) [6] are very similar at saturation coverages, the desorption of H₂ from Cu(111) occurs with a peak at 300 K and a shoulder at 230 K, more than 100 K higher than on Ag(111). On Cu(111), it has been suggested that subsurface binding sites for atomic hydrogen exist [6]. On Ag(111), the *absence* of a long “tail” on the high temperature side of the TPD peak [25] suggests that subsurface hydrogen is not important. Further evidence which argues against the subsurface H comes from the study of the hydrogen implanted in Ag(111) [26]. Implanted hydrogen on Ag(111) desorbs as a *peak* near 500 K, and this peak is absent here.

The desorption peak temperature (T_p) for hydrogen on Ag(111) is unusually low, below 200 K with an activation energy (E_d) of 5.5 kcal/mol. It is not only lower than on close packed transition metal surfaces, for example Ni(111) [27] and Pt(111) [25], but also much lower than on close packed non-transition metal surfaces. On Al(111) [10], H₂ desorbs with T_p above 320 K and with E_d of about 16 kcal/mol. On Zn(0001) [9], H₂ desorbs at T_p above 300 K with E_d of 11.1 kcal/mol. Suppose that the d orbitals of non-transition metals play a negligible role in bonding with H and that the metal–H bond strength only depends on the overlap between metal sp orbitals and the H(1s) orbital. Since the energies of Ag sp orbitals are higher than those of Al and Zn, the overlap between relatively deep-lying H(1s) orbitals and the substrate sp orbitals may be smaller for Ag than for Al or Zn. If this proposal is correct, then the Au–H bond will be even weaker than Ag–H and Cd–H weaker than Zn–H. To test this idea, studies of the chemisorption of atomic H on Au(111) and Cd(0001) are needed.

Turning to the desorption *kinetics*, which are of central interest to us

because of their role in surface chemical reactions involving hydrocarbon fragments [26], we note that while second order kinetics is most common, there are other exceptions. On Ni(110) and Pd(110) [28–30], a nearly zero-order desorption for hydrogen has been reported and is associated with the presence of islands of a reconstructed (1×2) phase acting as reservoirs of hydrogen [30]. On the non-transition metal surfaces, zero or fractional order kinetics for hydrogen desorption has been observed, in this work and others [9,10], on the close packed surfaces even when reconstruction does not occur. We find no evidence in the literature pointing to reconstruction of Ag(111), and we regard it as an unlikely explanation. While, as discussed above, the island model for D_2 desorption from Ag(111) is intuitively pleasing, a better understanding of the H/Ag(111) surface structure will require a detailed LEED, HREELS, and angle-resolved UPS study.

We now turn to the isotope effect indicated in fig. 1. While readily detected, it is not strong and it shifts both the shoulder and main TPD peak by the same amounts. Isotope effects are fairly common in surface science, but the extent to which they shift TPD peaks varies widely.

Based on the activation energy of the desorption reaction ($5.5 \text{ kcal mol}^{-1}$ (H_2) and $6.4 \text{ kcal mol}^{-1}$ (D_2)), the dissociation of gas phase hydrogen ($104 \text{ kcal mol}^{-1}$ for H_2 and $106 \text{ kcal mol}^{-1}$ for D_2), and the fact that molecular hydrogen does not dissociate on Ag(111) at 100 K, we can set an *upper* limit on the Ag–H (D) bond energy. The energy barrier between the gas phase and dissociated chemisorbed hydrogen atoms must be at least 6 kcal mol^{-1} since dissociation does not occur at 100 K. Thus, the Ag–D bond energy can be no greater than 53 kcal mol^{-1} ($0.5 \times [106 + 6.4 - 6] \text{ kcal mol}^{-1}$) and the Ag–H bond energy no greater than 52 kcal mol^{-1} . This estimate falls just beneath an upper bound of $56.8 \text{ kcal mol}^{-1}$ calculated for Ag_3H [31].

4. Summary

In summary, focusing on the surface chemistry of hydrogen on Ag(111), we find that molecular deuterium and hydrogen desorption on Ag(111) follows fractional order kinetics with $E_d = 5.5 \text{ kcal/mol}$ for H_2 and 6.4 kcal/mol for D_2 . An upper limit of 53 (52) kcal mol^{-1} is derived for the Ag–D (Ag–H) bond strength. The weak bonding and the fractional order kinetics are consistent with the formation of islands of D (H) as a result of attractive lateral interactions. UPS indicates that there is, at most, a very weak interaction between the Ag d-band and H(1s) orbitals. There is a broad and weak hydrogen-derived peak at 7.3 eV in HeII UPS. Adsorbed Cl blocks D adsorption, and at high Cl coverage, alters D binding slightly. The results for coadsorbed Cl and D are interpreted in terms of widely varying local surface coverages of D.

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