Dynamics of recombinative desorption of H2 and D2 from Cu(110), Cu(111), and sulfurcovered Cu(111)
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Rotational and vibrational state distributions have been determined for $\text{H}_2$ and $\text{D}_2$ recombinatively desorbing from clean $\text{Cu}(110)$ and $\text{Cu}(111)$ surfaces in ultrahigh vacuum, and also from sulfur-covered $\text{Cu}(111)$. A $2 + 1$ resonanced-enhanced multiphoton ionization technique is employed. For clean copper the $(v'' = 1)/(v'' = 0)$ vibrational population ratio for both $\text{H}_2$ and $\text{D}_2$ is $\sim 50$ times greater than the value expected for an equilibrium ensemble at the surface temperature $T_s$ for desorption from $\text{Cu}(110)$ and $\sim 100$ times greater from $\text{Cu}(111)$. In contrast, for sulfur-covered $\text{Cu}(111)$, the $\text{H}_2 (v'' = 1)/(v'' = 0)$ ratio is $10$ to $100$ times less than for clean $\text{Cu}(111)$ at the start of permeation but recovers sharply about 45 min later to a value close to that measured for the clean surface. We find that the total near-surface sulfur concentration appears to remain constant over the same time period, but that the overlayer structure is radically altered.

I. INTRODUCTION

Hydrogen plays a ubiquitous role in the surface and bulk chemistry of solids. Some simple but diverse examples are the recombination of hydrogen atoms to form the $\text{H}_2$ molecule on dust grains within the interstellar medium, the embrittlement of metals by dissolved hydrogen, the interactions of hydrogen in problems of reactor wall integrity, the reversible and safe storage of hydrogen by metals for fuel applications, and the catalytic hydrogenation of olefins by platinum group metals. The importance of the dynamics of these reactions is reflected in the fact that the step involving transport of molecular hydrogen to and from the solid surface may proceed with state-specific rates varying by factors nearing 100. Of course, the dynamics of these processes have intrinsic appeal to the chemist, as well, because they are a manifestation of the potential energy surfaces associated with the motions of $\text{H}_2$, $\text{H}$, and the atoms of the solid.

A specific example of hydrogen-solid chemistry, expressed in Eq. (1), is the dissociative chemisorption of molecular hydrogen and the subsequent dissolution of $\text{H}$ atoms into a metal:

$$\text{H}_2(\text{gas}) + \text{M(solid)} \rightarrow 2 \text{M-H(adsorbed)} \rightarrow 2 \text{M-H(adsorbed)}.$$  

The reverse of reaction (1) is the permeation through and recombinative desorption from the metal. Often, dissociative chemisorption reactions have an associated activation barrier and exhibit strong variations of the sticking coefficient on incident molecular parameters such as kinetic energy and angle of incidence. When the sticking probability depends so strongly on the "dynamical variables," one expects that the desorption flux will exhibit molecular quantum state distributions which depart substantially from Boltzmann distributions at the metal surface temperature $T_s$. These departures reveal which molecular motions and configurations are selected or "filtered" by the activation barrier and, when detailed balance can be applied to reaction (1), which of these motions affect the dissociative adsorption probabilities.

We report here the study of the dynamics of the activated recombinative desorption of molecular hydrogen from well-characterized single-crystal Cu surfaces, both clean and sulfur-covered. Our focus is on the internal degrees of freedom of the desorbing molecules; specifically we measure the rotational and vibrational distributions directly following desorption. This choice is motivated by the fact that the dissociative adsorption probabilities have already been characterized with respect to the variation of incident angle and molecular kinetic energy. For the reverse process, recombinative desorption, velocity, and angular distribution measurements have also been made. Hence, for the first time we will have an indication of the role which each molecular degree of freedom plays in recombination on and subsequent desorption from a surface of known composition and geometric structure.

The adsorption of molecular hydrogen was first demonstrated to be activated and dissociative by Pritchard and coworkers who studied adsorption on evaporated copper films. They found isosteric heats of adsorption in the range of 10–12 kcal/mol (per mole of $\text{H}_2$) on these polycrystalline samples and an activation energy for dissociative chemisorption of approximately 9 kcal/mol. Later work by Balooch and Stickney demonstrated that the recombinative desorption flux of $\text{H}_2$ from the three low index faces of Cu exhibited angular distributions which were strongly peaked along the surface normal. These workers tentatively ascribed their observations to a model suggested originally by Lennard-Jones which involved a potential curve crossing between atomic and molecular potentials above the surface. A schematic illustration of this is presented in Fig. 1.

Supporting evidence was presented in a beautiful experiment by Balooch et al., who determined dissociative adsorption probabilities of $\text{H}_2$ and $\text{D}_2$ on the (100), (110), and (310) surfaces of Cu as functions of incident molecular velocity and angle. They found that the activation barriers to dissociative adsorption could be surmounted by the incident kinetic energy projected along the surface normal, suggesting that the barriers associated with the translational degree of
freedom were approximately one dimensional. This had originally been proposed by van Willigen. Values of 3, 5, and 5 kcal/mol for these barrier heights were assigned to the (110), (100), and (310) faces, respectively. Cardillo et al. then used the concept of detailed balance to predict the results of the former. More recently, Comsa and David have measured the velocity distributions of D2 recombiningly desorbing from the (111) and (100) faces of Cu following atomic permeation. They found that the correlation expected between velocity and desorption angle for the simplest one-dimensional barrier model, namely, velocity increasing with increasing angle from the surface normal, did not exist. They took this as an indication of subsurface recombination, a rather unorthodox view.

The presence of sulfur on otherwise clean metal surfaces has been known to dramatically alter the dynamics of recombinative desorption for a variety of systems. For example, the vibrational population ratio \( \langle \nu^+ = 1 \rangle / \langle \nu^+ = 0 \rangle \) of \( \text{N}_2 \) desorbing from polycrystalline iron increases sharply as an increasing function of sulfur coverage. In the present case, the vibrational population ratio of \( \nu^+ = 1 \) to \( \nu^+ = 0 \) of \( \text{O}_2 \) desorbing from Cu, saturation sulfur coverages have a substantial effect on desorption angular distributions but only change the mean kinetic energy of the desorption flux by \( \approx 5\% \). These results suggest that the distribution of hydrogen internal degrees of freedom may also be sensitive to sulfur contamination and we have undertaken a preliminary study of this question on the Cu(111) surface.

II. EXPERIMENTAL

A schematic diagram of the apparatus is depicted in Fig. 2. The vacuum chamber and associated pumping procedures have been previously described. Recombinative desorption fluxes of \( \text{H}_2 \) and \( \text{D}_2 \) are provided by atomic permeation from a 1–3 atm gas line through heated single-crystal copper sample membranes having nominal thicknesses of 0.5 mm. Sample cleanliness and geometric order are accomplished by Ar+ bombardment and annealing cycles and are verified by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), respectively. The desorption flux is crossed by a focused laser and is ionized via resonance enhanced 2 + 1 multiphoton ionization (REMPI). \( \text{H}_2^+, \text{D}_2^+ \), and background gas ions are extracted into a time-of-flight mass spectrometer. Ions are detected with a high-gain multiplier array as a function of laser wavelength to obtain an ionization spectrum. Analysis of the vibrationally and rotationally resolved line intensities allows the rovibrational state distributions of molecular hydrogen desorbing from clean and sulfur-covered copper surfaces.

Figure 3 presents three views of the sample permeation source. It consists of a single-crystal 99.999% pure Cu cylinder having 1.25 cm diameter and length and containing an interior 3 mm channel electrode discharge milled to within 0.8 mm of the oriented front face. The front face is oriented to within 1° of the (110) face as quoted by the crystal manufacturer (Monocrystals Co., Cleveland, OH). Electrodischarge milling was chosen for channel construction to avoid creating defects in the sample substrate, a problem to which copper is extremely susceptible due to its softness. The (111) sample source was constructed using a slightly different procedure in which an oriented (1°) 99.999% purity 1 cm diameter, 1 mm thickness disk was electron beam welded to a channeled, 99.999% purity cylinder identical in design to that illustrated in Fig. 3. After welding, the disk was sanded carefully and chemically etched to a final 0.3 mm thickness.
We have employed a $2 + 1$ resonance-enhanced multi-photon ionization technique to determine rovibrational state distributions of recombinatively desorbing $\text{H}_2$ ($\text{D}_2$). Laser ionization wavelengths at $\lambda_1 = 193 \text{ nm}$ and $\lambda_2 = 211 \text{ nm}$ are generated by stimulated Raman scattering in $\text{H}_2$ gas using the focused output of a frequency-doubled pulsed dye laser. The dye laser is pumped with the second harmonic of a Nd$^3+$: YAG laser (Quanta-Ray DCR-1A). The total undispersed and recollimated output of the Raman cell passes through a rotatable Brewster window and is focused into the desorption flux normally along the surface normal and approximately 1.25 cm from the surface. Ions are formed between two plates which function as the time-of-flight mass spectrometer extractor. Ions of different mass are separated by virtue of their flight times, which vary as the square root of the mass. The ions eventually pass through a grid and strike a charged particle detector (Galileo FTD 2002). The dye laser is scanned in wavelength while the output of the detector is collected via gated integration (LeCroy 2249SG and 2323) to obtain an ionization spectrum. Typically, a spectrum requires 45 min to collect, and three are acquired sequentially before sample recleaning. During this time a small amount of carbon accumulates on the sample but does not affect the distributions.

Two pyroelectric detectors are used to simultaneously record the power spectra of the beamsplit and dispersed $\lambda_1$ and $\lambda_2$ during a scan. Power normalization is accomplished by dividing the measured $\text{H}_2$ and $\text{D}_2$ Q-branch line intensities by the product of the $\lambda_1$ and $\lambda_2$ intensities.

III. RESULTS AND DISCUSSION

A. Clean Cu(110), Cu(111)

Figure 4 shows representative ionization spectra of $\text{H}_2$ produced in (a) recombinative desorption from Cu(111) at 850 K and (b) a heated tungsten free jet at a stagnation temperature $T_0$ of 1700 K. We use the free jet to verify the accuracy of the ionization technique for determining rotational populations, and also to calibrate the relative $v^* = 0$ and $v^* = 1$ intensities against a known population standard. This figure immediately demonstrates the pronounced vibrational excitation of the desorbing $\text{H}_2$ molecules compared to that expected for an equilibrium ensemble at 850 K. For example, the $(v^* = 1)/(v^* = 0)$ population ratio at $T_0 = 1700$ K would be $\sim 34$ times greater than the ratio at 850 K. In contrast, inspection of the desorption data shows this ratio (averaged over $J$) to be only slightly less than that of the calibration beam. More detailed analysis$^{23}$ shows that the actual $(v^* = 1)/(v^* = 0)$ ratios in desorption are $0.084 \pm 0.030$ and $0.35 \pm 0.20$ for $\text{H}_2$ and $\text{D}_2$, respectively, from Cu(111). On the (110) surface these ratios are $0.052 \pm 0.014$ for $\text{H}_2$ and $0.24 \pm 0.20$ for $\text{D}_2$. In contrast, the vibrational population ratios in equilibrium at $T_e = 850$ K are 0.0009 for $\text{H}_2$ and 0.0063 for $\text{D}_2$, so that recombinative desorption of molecular hydrogen yields 50–100 times more vibrational excitation than the equilibrium result.

Rotational distributions have been discussed elsewhere$^{22,23}$ and we simply present them in Fig. 5 for completeness. Note, however, that this degree of freedom is also
spectrum in (a) corresponded to a Boltzmann distribution at relative strength of spectra of H$_2$. (a) Spectrum of H$_2$ recombinatively desorbing from the surface. In addition, insensitivity of the rotational distributions to surface structure suggests that recombination occurs at distances sufficiently far above the surface atom plane so that surface-structural modulation of the H$_2$-surface repulsive potential is weak.

B. Sulfur-covered Cu(111)

Early experiments in our laboratory suggested that sulfur contamination of the copper surfaces causes profound changes in the observed vibrational population ratios. More detailed population determinations, coupled with sulfur overlayer structure and concentration studies, have been undertaken on Cu(111) to characterize further this interesting behavior.

Sulfur is supplied to the surface via a molecular beam of H$_2$S. Uniform coverage is accomplished by sample manipulation within the beam over the course of the 30 min exposure. Exposures are made at surface temperatures ranging from 500 to 800 K. AES data are shown in Fig. 6, for both clean Cu(111) and Cu(111) with a saturation coverage of sulfur. As shown in Fig. 7, the presence of sulfur has a dramatic effect on the apparent vibrational population ratio, evidenced by the drastic diminution of $Q_3(0,1)$ ($v''=1$) intensity relative to that of $Q_3(0,0)$ ($v''=0$). Concurrent with the $Q_3(0,1)$ diminution is a reduction of the overall desorption rate into the vacuum chamber, shown in the inset. For clean Cu(111), the steady-state pressure increase during permeation is approximately $3 \times 10^{-9}$ Torr whereas the sulfur-covered surface desorption rate is such that the pressure increase is a mere $1 \times 10^{-10}$ Torr. Over a 2 h period, however, the pressure increase climbs to 55% of the clean-surface value when $T_s$ is fixed at 850 K. Figure 7 graphically charts the restoration of the $Q_3(0,1)/Q_3(0,0)$ signal ratio to values approximately equal to those for clean Cu(111). Also plotted is the simultaneous gradual increase in the overall desorption rate. Although the overall desorption rate shows a smooth increase, the recovery of the desorption rate into the vacuum chamber, shown in the inset. For clean Cu(111), the steady-state pressure increase during permeation is approximately $3 \times 10^{-9}$ Torr whereas the sulfur-covered surface desorption rate is such that the pressure increase is a mere $1 \times 10^{-10}$ Torr. Over a 2 h period, however, the pressure increase climbs to 55% of the clean-surface value when $T_s$ is fixed at 850 K. Figure 7 graphically charts the restoration of the $Q_3(0,1)/Q_3(0,0)$ signal ratio to values approximately equal to those for clean Cu(111). Also plotted is the simultaneous gradual increase in the overall desorption rate.
ions employed during our REMPI experiment while monitoring data from AES and LEED. Surprisingly, no significant change in the ratio of 152 eV sulfur to 105 eV copper peaks is noted during the desorption flux recovery period, implying that the near-surface sulfur concentration remains constant. The overlayer structure, on the other hand, changes dramatically during hydrogen permeation but is stable over the same period in the absence of hydrogen permeation. The LEED pattern obtained after H$_2$S exposure but before permeation is identical to that already published and is presumed to represent a saturation coverage of $7.86 \times 10^{14}$ atoms/cm$^2$. The overlayer structure is thought to have the geometry shown in Figs. 12 and 13 of Ref. 25. After permeation the LEED pattern becomes very diffuse with low contrast 1 X 1 substrate spots situated in a field of weak streaks, probably a highly disordered form based nominally on the original net. We find tentatively that the degradation in overlayer order occurs much more rapidly ($\sim$ 10 min) than do the changes in desorption rate and dynamics ($\sim$ 45 min) charted in Fig. 7.

Finally, an attempt was made to detect the possible evolution of the SH molecule using REMPI. However, no sulfur-containing masses were ever observed in the mass spectrum, consistent with our observation that the sulfur coverage remains constant during permeation for the conditions employed.

While it is not yet possible to unravel fully the factors controlling the complex changes noted in the desorption dynamics from sulfur-covered Cu(111), several comments are pertinent. The total concentration of sulfur detected by the Auger spectrometer (which presumably averages over several near-surface layers) does not sensitively mirror the changes in the dynamics. There remains a slight chance that sulfur begins to diffuse away from the outermost surface layer and into the near-surface region but the high temperature LEED results obtained without hydrogen permeation argue against this. It is clear that radical changes in the overlayer structure occur only during permeation of hydrogen. Whether this structural disordering is responsible for the eventual restoration of the $Q_2(0,1)$ intensity relative to that of $Q_2(0,0)$ after saturating the surface with sulfur, or whether both observations are simply manifestations of a broader common change, is unclear. Perhaps the accumulation of hydrogen near the surface during the period of diminished desorption rate plays a key role in both events.

A most striking aspect of the sulfur-covered copper results is the unambiguous and radical change in desorption dynamics manifested by a decrease in vibrational excitation of the desorbing H$_2$ shortly after copper exposure to H$_2$S. Several compelling implications are suggested immediately if one extends the ideas of detailed balance already applied to the clean Cu-H$_2$ system. First, the probability of dissociative adsorption for H$_2$ molecules in $v'' = 1$ is inferred from our data to be $\sim$ 50 times greater than for molecules in $v'' = 0$ on Cu(110) and $\sim$ 100 times greater on Cu(111).
contrast, it is inferred that the relative \(\langle\psi\rangle^2 = 1 / \langle\psi\rangle^2 = 0\) dissociative adsorption probability ratio for \(\text{H}_2\) has an upper limit of \(\sim 10\) (and is likely to be less) on sulfur-covered Cu(111). The contamination of Cu(111) by sulfur therefore causes a tenfold to 100-fold decrease in the relative quantum state-specific adsorption rates. This behavior is qualitatively opposite to that exhibited by sulfur on other gas–metal systems. The trends have usually been for sulfur contamination to increase the observed departures from “thermal” behavior, i.e., distributions characterized solely by \(T_s^{16}\).

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20G. Golovchenko (private communication).