Absorption of H_2 and D_2 on W (110) surface at liquid-helium temperature

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Weakly bound states of a molecular adsorption of hydrogen, with desorption temperatures ~5, 8, and 60 K, have been observed. Atomic adsorption states as well as molecular states are populated at $T \sim 5$ K. The formation of the molecular state with 8 K broadens the angular distribution of scattered molecules.

Research on the adsorption of hydrogen on the surfaces of transition metals is of considerable interest for applications and for fundamental science. Several processes—heterogeneous catalysis involving hydrogen, the storage of hydrogen in metals as an ecologically clean fuel, the hydrogen embrittlement of metals, etc.—all include a chemisorption of hydrogen as a major step. The very small size and mass of the hydrogen atom (and molecule) make this adsorbate "sensitive" to features of the atomic and electronic structure of the surface which are inaccessible to larger adatoms. The small mass of hydrogen would lead us to expect manifestations of quantum effects in the kinetics of phase transitions in the adsorbed layer at low temperatures.

Although the adsorption of hydrogen on the surfaces of transition metals has generally been studied quite comprehensively,[1] the adsorption at very low substrate temperatures ($T \lesssim 20$ K) is an exception to this rule. Only a few studies of the behavior of adsorbed hydrogen and deuterium layers at T close to liquid-helium temperature have been published.[2–6] For the most part, these studies have dealt with phase transitions and the mobility of adatoms. They have not contained direct data on the populations of weakly bound adsorption states. Such information is required for a reliable interpretation of low-temperature experiments with adsorbed layers.

Our purpose in the present study was to learn about weakly bound adsorption states of hydrogen and deuterium and the kinetics of the filling of these states on the W (110) surface. We used the technique of molecular beams and thermodesorption spectroscopy with time-of-flight detection of the desorbed particles.[7] The axis of the molecular beam was directed along the normal to the surface of the sample. The scattered (and desorbed) molecules were detected in a solid angle of 0.2π sr. The axis of the detection cone made an angle of 45° with the normal.

Figure 1 shows the thermodesorption spectrum of hydrogen recorded after adsorption at $T \sim 5$ K to the point of saturation. In this spectrum we see four adsorption states, with thermodesorption peaks at 8, 60, 410, and 550 K. The last two states have been seen previously,[8] while the states at 8 and 60 K are being seen here for the first time. In Fig. 1 we also see indications of an even lower-temperature state, with ~5 K, in the form of a decrease in the ion current of the detector when the molecular beam is

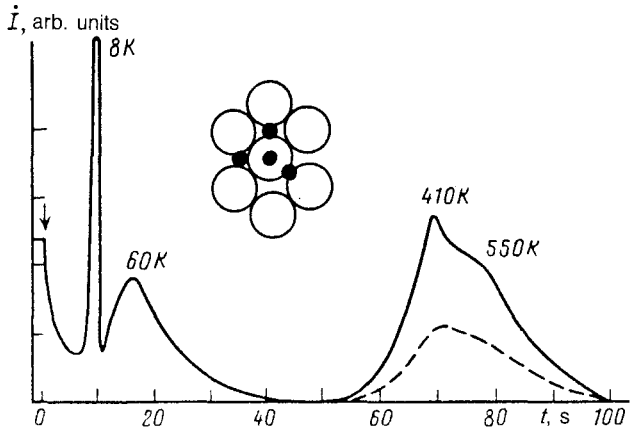

FIG. 1. Hydrogen thermodesorption spectrum. The arrow shows the time at which the molecular beam was blocked, and the heating of the sample was begun. The open circles in the inset are W atoms, and the filled circles H_2 molecules.

blocked for a time much longer than the resolving time of the apparatus.

The nature of the observed absorption states has been identified by an isotope-exchange method. Specifically, an $H_2 + D_2$ beam was directed at the target, and the thermodesorption of HD molecules was measured. The dashed line in Fig. 1 is the thermodesorption spectrum of HD. There are no low-temperature HD peaks; this result is evidence of a molecular form of the adsorption in these states. The isotope exchange in the states with 410 and 550 K is evidence of a dissociative form for the adsorption (in agreement with Ref. 8).

Lines 1–4 in Fig. 2 show the kinetics of the filling of various hydrogen absorption states on the W (110) surface at ~ 5 K. The atomic adsorption states with 550 and 410 K are filled in succession. The molecular state with 60 K begins to be filled at the same time as the state with 550 K; it reaches saturation along with the state with 410 K. The molecular state with 8 K begins to be filled after a significant filling of the other states.

According to Ref. 9, no dissociative adsorption of hydrogen occurs on W (110) at $T \lesssim 60$ K, so we are obliged to assume that the peaks with 410 and 550 K in Fig. 1 have resulted from a conversion of molecular hydrogen with increasing T. However, the results of the following experiment show that this is not the case. Molecular adsorption states were formed on the W (110) surface with atomic states filled beforehand (at $T \sim 100$ K). The plus signs in Fig. 2 show the growth of the molecular states at $T \sim 5$ K on this surface. We see that the hydrogen content in the molecular states does not depend on whether atomic states are present (as in the first experiment). An agreement of this sort would not have been possible if some of the molecular phase were consumed in the formation of the atomic phase.

We thus conclude that atomic and molecular states form in parallel on the W

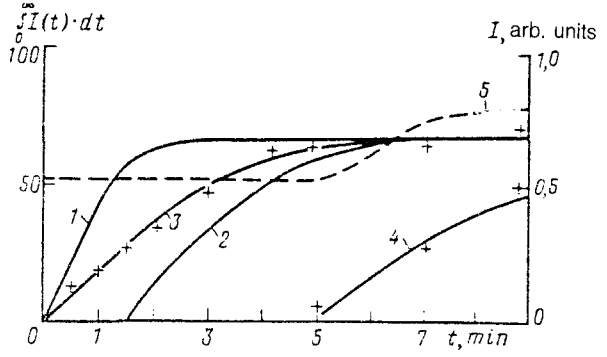

FIG. 2. Kinetics of the filling of hydrogen adsorption states. 1—550 K; 2—410 K; 3—60 K; 4—8 K; 5—ion current of the scattered-molecule detector.

(110) surface at $T\sim 5$ K. In other words, the activation barrier for a transition to a dissociated state is very low for some of the H_2 molecules, while it is substantial for the rest. We can explain why molecules find themselves in different situations on the basis of a significant diversity in the likely adsorption sites on the W (110) surface (as shown in the inset in Fig. 1). The reason why the activation barrier for a transition of H_2 to a state of dissociative chemisorption is low may be a suppression of the Pauli repulsion, itself a result of a redistribution of electrons between *s* and *d* states of the metal.[10]

Curve 5 in Fig. 2 also shows the ion current of the scattered-molecule detector versus the duration of the exposure of the sample to the hydrogen flux at ~ 5 K. We see that, as the molecular state with 8 K becomes filled, the ion current of the detector increases noticeably. The reason for this increase may be a change in the angular distribution of the scattered molecules, from nearly specular to cosinusoidal. We know that hydrogen molecules are scattered in a nearly specular fashion by atomically smooth metal surfaces,[1] and the formation of a "cushion" consisting of a layer of physically adsorbed molecules might be quite capable of disrupting this specular scattering. One cannot, of course, rule out the possibility of diffraction effects, since a hydrogen layer adsorbed at such a low temperature would have some ordered structure.[2]

The results found on the adsorption of D_2 are essentially the same as those on H_2.

Let us summarize the results of this study. (1) Weakly bound adsorption states of molecular hydrogen with desorption temperatures ~ 5, 8, and 60 K have been observed. (2) At $T\sim 5$ K, hydrogen adsorbs in both molecular and atomic form. (3) The angular distribution of scattered hydrogen molecules broadens as the molecular adsorption state with the desorption temperature of 8 K becomes filled.

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