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PHOTOEMISSION FROM CONDENSED LAYERS OF H2 ON CU AND AU.(U)
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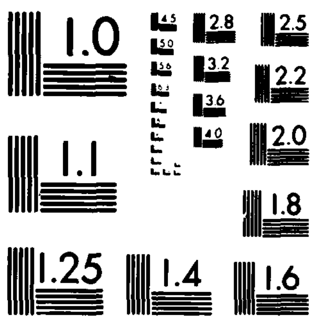

MICROCOPY RESOLUTION TEST CHART

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PHOTOEMISSION FROM CONDENSED LAYERS OF H_2 ON Cu AND Au

by

W. Eberhardt, R. Cantor, F. Greuter and E. W. Plummer

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W. Eberhardt and R. Cantor
Brookhaven National Laboratory, Physics Department, Upton, New York 11973

and

F. Greuter and E. W. Plummer
University of Pennsylvania, Department of Physics and Laboratory for Research on the Structure of Matter,
Philadelphia, Pennsylvania 19104

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We have measured the photoemission of monolayers as well as thick films of H_2 molecules condensed onto Cu and Au. The adsorbed monolayer exhibits a relaxation energy of 1.75 eV whereas we see a bandlike 1s state for thick layers having a bandwidth of 1.2 eV. We also observe energy loss features which are in agreement with previous electron energy loss and optical absorption studies.

Hydrogen is known to adsorb in atomic form on many transition metals having not completely filled d-bands.[1] We here report the first photoemission measurements of molecular hydrogen adsorbed onto Cu and Au at 4 K. We have no indication that the H_2 molecule dissociates upon contact with the metal, but rather the molecule is very weakly bound and desorbs upon very slight warming to about 15 K. Atomic hydrogen on Cu has almost the same binding energy as on Ni,[2] and one would therefore expect the desorption to start around 250 K. This manifests the existence of a so-called "dissociation barrier" on noble metals having a filled d-band which the H_2 cannot overcome even though the gas is at room temperature prior to the adsorption. Previous molecular beam scattering studies have measured the threshold for dissociation adsorption to be 5 kcal/mol on Cu(100), way above the thermal energies of H_2 at room temperature.[3]

The second point of interest in these data is related to the prediction of a metallic phase of solid H_2 at high pressures.[4] We here can test the band structure calculations of solid H_2 at least in the low or zero pressure limit, by comparing the data of a thick H_2 film with the calculation by Friedli and Ashcroft.[5] Until today only optical adsorption[6,7] and electron energy loss data[8] exist which are related to the band structure only indirectly by measuring transition energies between occupied and unoccupied bands or excitonic states.

The experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin using a toroidal grating monochromator (TGM)[9] and a commercial double pass cylindrical mirror electron analyzer (PHI model 15-255). The Cu (100) crystal was clamped onto a Cu dewar and cleaned in situ by Ar ion bombardment and subsequent annealing. Au was later evaporated onto this crystal and the measurements were repeated using these polycrystalline Au films as a substrate. The pressure of the system before H_2 deposition was about 5×10^{-11} Torr. Thus we were able to keep our sample free of contaminants for more than one hour even at these low temperatures. We should add a remark about the temperature of the crystal during our experiments. The crystal was 1/2 mm thick and all its back surface was in contact with the He reservoir of the dewar. This reservoir was pumped by a forepump so that the temperature of the liquid He was certainly less than 4 K.

Judging from the vapor pressure curves of solid H_2 [10] and the fact that we maintained a pressure of about 5×10^{-10} Torr in our chamber after deposition of a thick H_2 film we estimate the temperature to be 4 ± 1 K during the experiments. We observed a saturation of the film thickness after deposition of about 5 monolayers of H_2. We attribute this saturation effect as being due to a balance between the radiative heat coming to the film from the outside and the thermal conductivity through the film from the dewar.

Figures 1 and 2 show angle integrated energy distribution curves taken at 30, 35 and 40 eV photon energy after monolayer (1 L) and multilayer (5 L) adsorption of H_2. Monolayer adsorption results in a H 1s peak at a binding energy of 9.2 eV with a FWHM of 0.9 eV (dashed curves). A thick H_2 layer shows a very broad (2.1 eV FWHM) peak the center of which has moved approximately 1.2 eV to higher binding energy compared to the first layer. This peak also weakly indicates a doublet structure.

A binding energy of 9.2 eV for the H_2 level in the first adsorbed layer indicates an extra atomic relaxation energy of 1.75 eV, if we assume a work function of 4.5 eV. This magnitude of the extra atomic relaxation energy is not unusual. The measured value of the binding energy (9.2 eV) is also consistent with the hydrogen being adsorbed as molecular species. Atomic hydrogen would have a binding energy of 7.4 eV if the extra atomic relaxation was the same. The layer desorbs around 10-15 K, again a strong evidence for molecular H_2.

The measured width of the H_2 1s level of 0.9 eV FWHM with respect to less than 50 meV in the gas phase[11] deserves several remarks. We can account for this remarkable increase in linewidth by a decrease of the hole lifetime due to interatomic Auger processes involving substrate electrons. This effect causes the linewidth of, for example, chemisorbed atomic hydrogen on Ni, Pd or Pt to broaden to 1.1 to 1.2 eV.[1] Naturally, for a physisorbed H_2 molecule the interaction with the substrate is weaker and accordingly the broadening not quite so strong. An Anderson Newins type initial state broadening[12] can be excluded as explanation for the linewidth since the level is split off the bottom of the s-p band by 0.4 eV on Cu (100) and even more on an Au substrate, so that there exist no energetically degenerate substrate states to interact with the H_2 1s orbital. Inhomogeneities in the film could contribute a small amount to the broadening ($\leq$0.4 eV) as we found in previous studies.[13]

In the above paragraph we have just explained the relatively large linewidth of the H_2 1s level in the adsorbed phase. However in gas phase photoemission vibrational sidebands are observed,[11] which upon broadening of the individual lines would give rise to a smeared out Franck-Condon envelope with 1.5 eV FWHM. Therefore we now have to wonder why the observed linewidth of the adsorbed molecule is so much smaller than the convoluted gas phase photoemission. This clearly indicates higher order vibrational sidebands are drastically damped upon contact of the adsorbate with the metal surface. Thus the overall lineshape of the Franck-Condon envelope changes and naturally the width too. Gadzuk[14] has predicted this behavior in theory as being caused by coupling of the vibronic excitations of the molecule to energetically degenerate excitations of the nearly free electron gas of the substrate.

In the following we are going to discuss the photoemission results of the thick H_2 films. Judging from the H_2 1s intensity and the decrease of the Cu d band emission we estimate the thickness between 3 and 5 layers. Compared to the monolayer the H_2 1s peak shifts by about 1 eV to higher binding energ. Simultaneously the peak broadens and exhibits a weak but recognizable doublet structure. Crystalline Hydrogen has, according to theory,[5] occupied bands with a total width of 1.37 eV and a high density of states at the top of the band. This filled band of solid crystalline H_2 would in principle cause a photoemission signal just as we observe it from the films we have studied. However, the position of the Fermi level would coincide just about with the bottom of the conduction bands of solid crystalline H_2 and definitely not at midgap as one might expect. We know the size of the bandgap from experiment and theory. The onset for optical transitions occurs at 11.2 eV,[6] whereas the calcualted gap is with 9.2 eV even smaller. Therefore, the location of E_F at the bottom of the conduction band is surprising and could only be explained by charge transfer from the Cu substrate into the H_2 film. We are completely aware of the second possible explanation for the structure in the H_2 1s peak. In principle this kind of appearance could be caused by different screening of the hole depending on the distance to the metal substrate.[15] The layers closest to the metal atoms would show the largest screening and therefore the smallest observed binding energy. Typically the binding energy as measured in photoemission would increase by about 1 eV comparing the first layer and bulk solid H_2. This could very well explain the doublet structure we observe for thick H_2 films. However we reject this explanation for the following two reasons: First, the intensity of the shoulder does not decrease with increasing film thickness as could be expected if it would be the emission of the layer in contact with the substrate and second, the relative intensity of the shoulder compared to the higher binding energy peak is largest for excitation with 70 eV photons, when the escape depth is probably close to the minimum. Again, if the emission of the layer in contact with the substrate was causing this shoulder, we would expect it to be larger for lower photon energies (kinetic energies) when the escape depth is larger and not most intense at the shortest escape depth. Therefore we think that the doublet structure in the H_2 1s emission resembles the photoemission of bandlike states of solid H_2 and is not caused by a difference in screening.

Figure 3 shows a spectrum of a thick H_2 layer taken at a photon energy of 70 eV. Besides the previously discussed peak at about 10 eV binding energy we observe at least two rather broad peaks centered at 16.5 and 21 eV binding energy. We attribute these structures as being characteristic electron energy loss features originating from the Cu d-band photoelectrons being scattered in the hydrogen film. Electron energy loss data of solid H_2 exhibit a rather strong peak at 14 eV with a width of 1 eV.[8] The electron loss data do not extend beyond 16 eV, but comparing our data with the optical absorption data available we find strong absorption structures for solid H_2 or D_2 films at 13.4 and 17.4 eV.[6,7] The transitions causing these adsorption peaks are assigned to excitonic excitation (13.4 eV) and interband transitions (17.4 eV).[7] Both of these transitions can be excited by electrons also, so that we can explain the two peaks in the electron energy loss of the directly excited Cu 3d electrons we observe. The spectra we obtain after H_2 deposition on Au exhibit the same features, as shown in Fig. 4. The H_2 1s peak is shifted altogether about 0.5 eV closer to E_F, but still shows a doublet structure. The loss features are present too, but less distinct, because the Au d bands are wider and therefore the loss structures overlap and appear to be smeared out and structureless.

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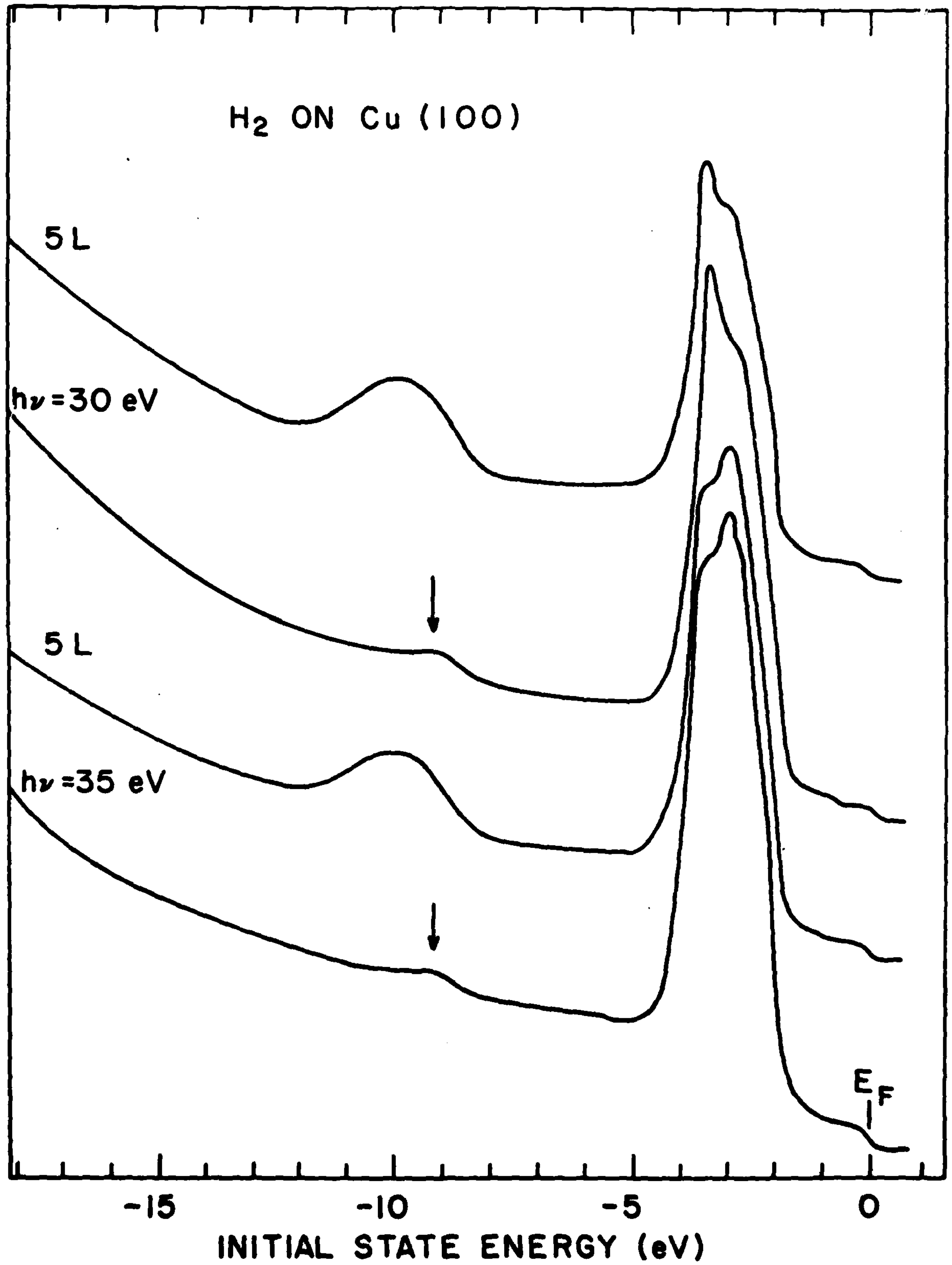
Figure Captions

Figure 1. Angle integrated photoemission EDC's from a monolayer H_2 film (about 1 L exposure) and a thick H_2 film (5 L) taken at 30 eV (35 eV) photon energies for the top (bottom) curves.

Figure 2. EDC's of clean Cu (100) and after H_2 adsorption for monolayer (dashed curve) and higher coverage (5 L exposure). The top curve also indicates one of many possible deconvolution of the H_2 peak into a peak and a shoulder.

Figure 3. Photoemission of a thick H_2 film on Cu showing not only the direct H_2 1s emission but also characteristic energy loss features.

Figure 4. H_2 condensed onto Au showing the 1s derived state and characteristic loss features of the Au d-band emission.



H2 ON Cu (100)
5 L
hν=30 eV
5 L
hν=35 eV
EF
-15
-10
-5
0
INITIAL STATE ENERGY (eV)

FIGURE 1

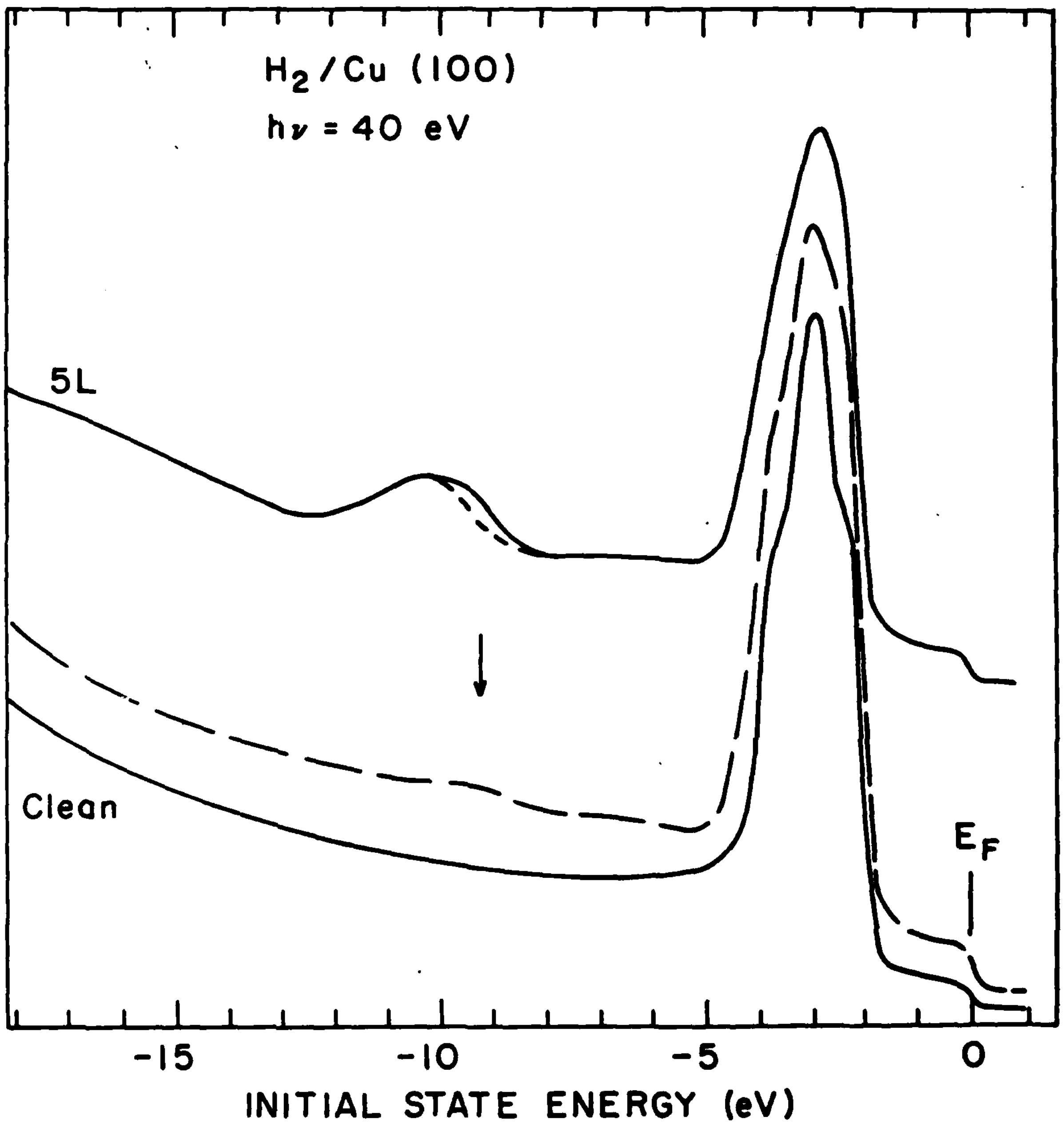
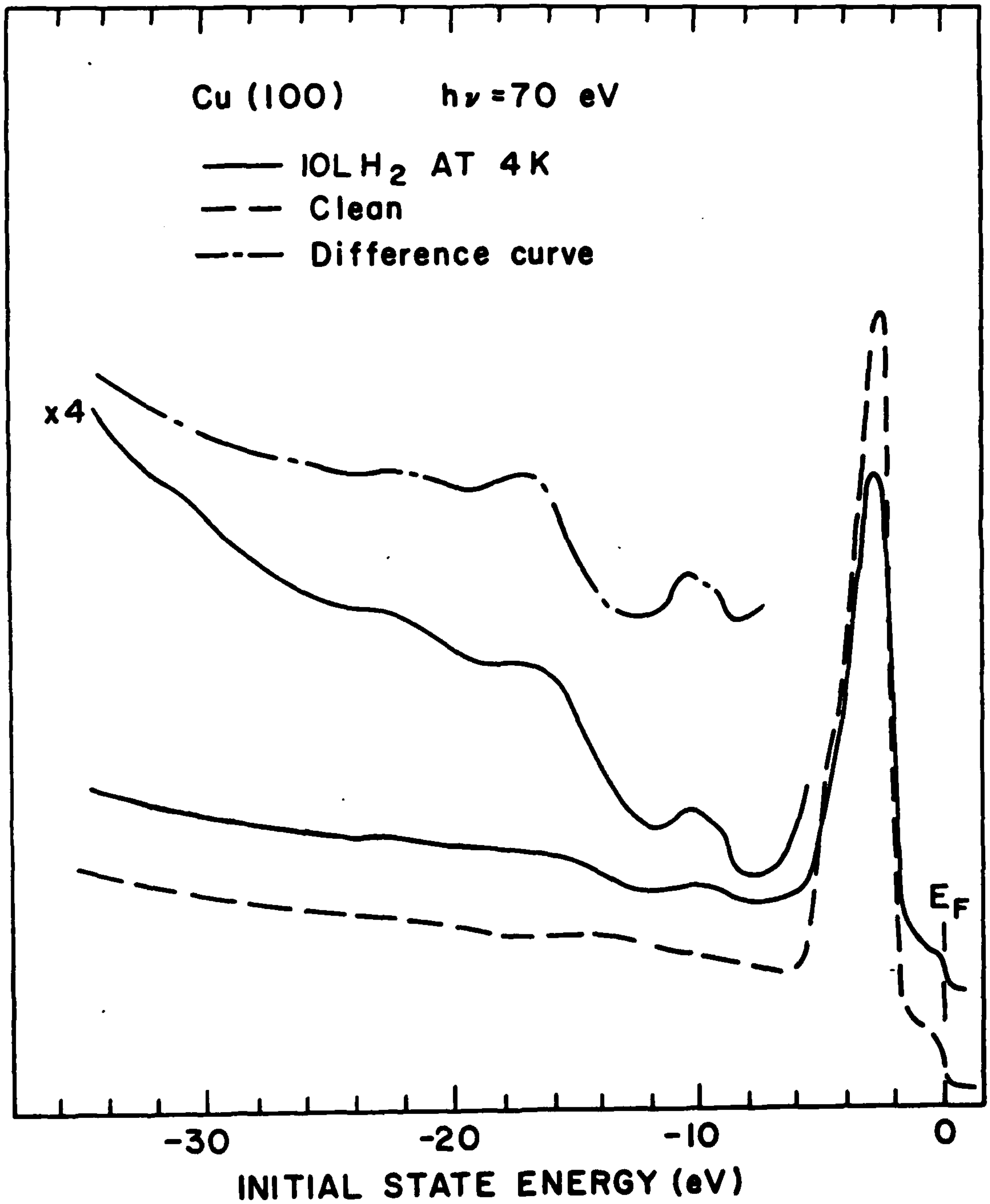


FIGURE 2



Cu (100)
hν = 70 eV
10L H2 AT 4K
Clean
Difference curve
x4
EF
-30
-20
-10
0
INITIAL STATE ENERGY (eV)

FIGURE 3

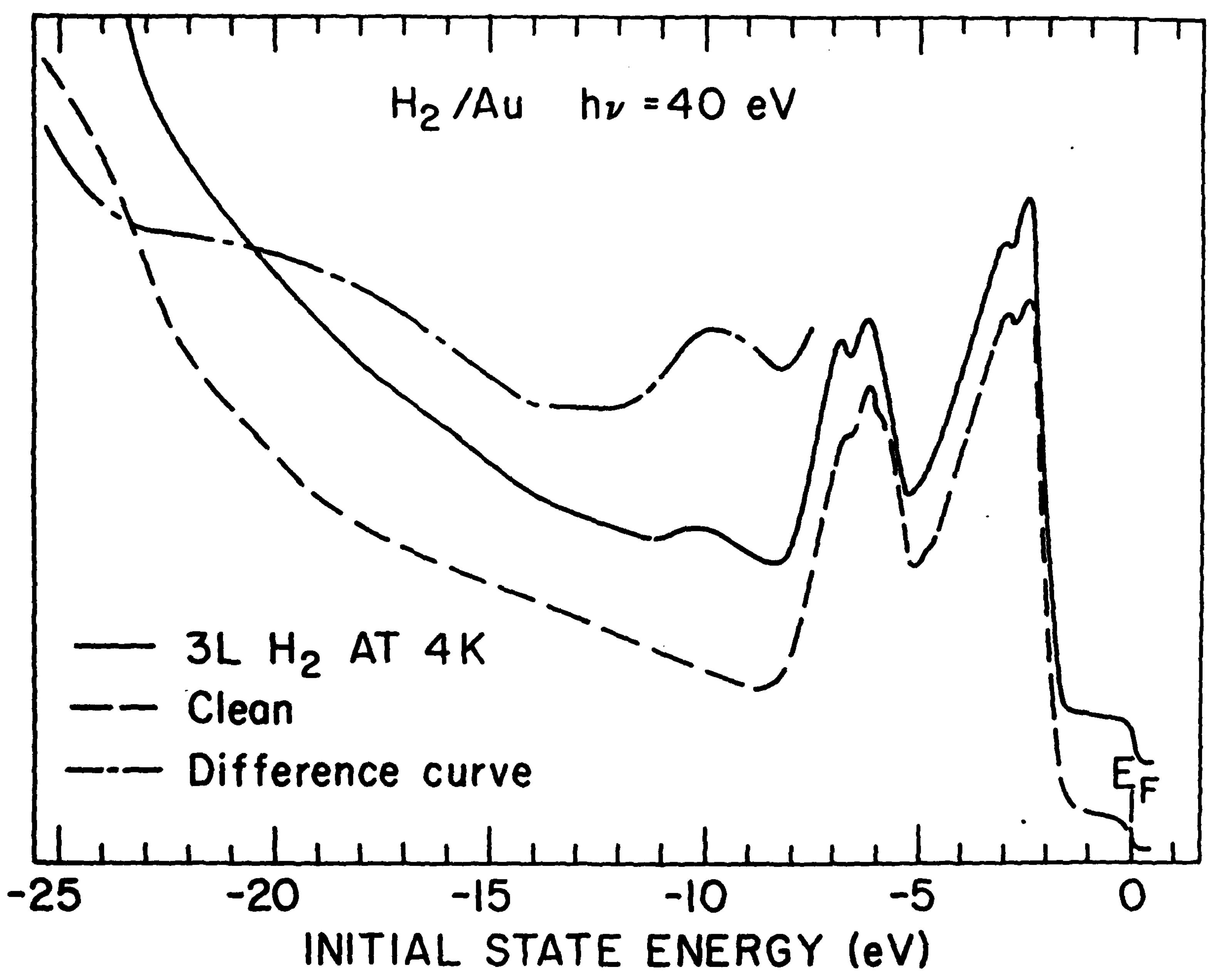

H2 /Au hν =40 eV
3L H2 AT 4K
Clean
Difference curve
EF
-25
-20
-15
-10
-5
0
INITIAL STATE ENERGY (eV)

FIGURE 4

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