

INFRARED STUDIES OF LOW-TEMPERATURE ADSORPTION OF H₂ ON ZnO

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Spectra recorded at 4-77 K evidence the existence of several IR active forms of dihydrogen adsorbed on ZnO. Studies of the effect of surface hydration and preadsorption of CO on the spectra of adsorbed hydrogen indicate difference in the sites of molecular and dissociative H₂ adsorption.

ИК-спектры, полученные при 4-77 К обнаруживают существование нескольких активных в поглощении форм молекулярно адсорбированного на ZnO водорода. Исследование влияния гидратации поверхности и предварительной адсорбции СО на спектры водорода показывает различие центров молекулярной и диссоциативной адсорбции H₂.

IR spectroscopy studies have revealed that at low temperatures hydrogen adsorption on ZnO is mainly of two types: dissociative and molecular. The former can be identified by two characteristic bands at about 3500 and 1700 cm⁻¹ attributed to OH and ZnH groups, respectively /1-3/. The latter is characterized by a band at 4019 cm⁻¹ observed in the presence of gaseous H₂ at 77 K and attributed to chemisorbed H₂ molecules /4/. Both molecular and dissociative adsorptions are suggested /4/ to take place on the same sites, whose nature is not yet clear.

We have studied the IR spectra of H₂ adsorbed on ZnO at 77 K and 4 K in a cell described previously /5/. In each step of sample dehydration, besides H₂ adsorption, we have also examined spectra of CO adsorbed at 77 K which is a convenient test molecule for the presence of certain surface sites. Spectra were recorded on a UR-20 spectrophotometer. In some experiments a glass filter was inserted before the cell in order to decrease the heating of the sample by the infrared beam. While the cell was cooled by liquid helium, 3-5 torr of gaseous He was admitted to the sample for ensuring better thermal contact with the cold walls. The spectral width of the slit was not more than 30 and 10 cm⁻¹ for the bands at 4000 and 3000 cm⁻¹, respectively.

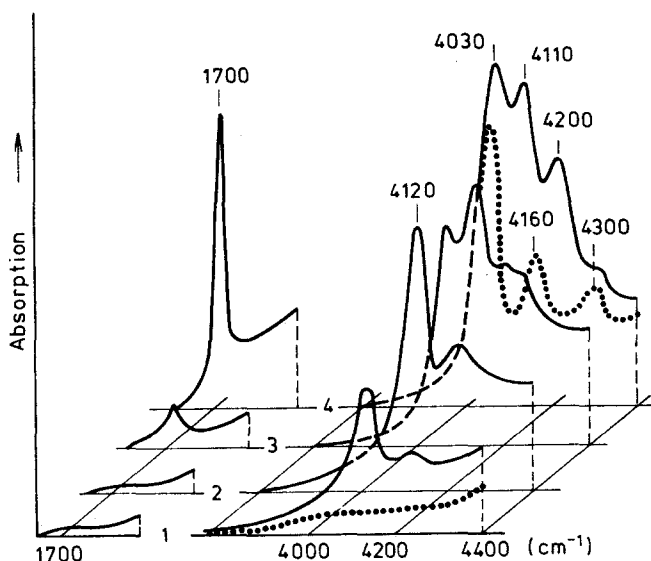


Fig. 1. H_2 adsorption on ZnO, dehydration at 293 (1), 473 (2), 623 (3) and 723 (4). Spectra were recorded at 4 K (full line) and 77 K (dotted line). Maximum at 4300 cm^{-1} (curve 4) belongs to the combined OH frequency

1–2 g batches of commercial ZnO powder ($S \sim 10.5\text{ m}^2/\text{g}$) were pressed into $10 \times 30\text{ mm}$ plates. To clean the surface, samples were calcined first in oxygen and then in vacuum at 750 K for 1 h. If necessary, they were hydrated in water vapor and evacuated at a temperature depending on the required degree of surface hydroxylation. If the temperature of evacuation was higher than 500 K, samples were cooled in 1–2 Torr of oxygen to prevent their reduction significantly decreasing their transparency in the IR region.

ZnH and HH vibration regions of the spectrum of hydrogen adsorbed on ZnO which was evacuated at various temperatures after contact with water vapor, are illustrated in Fig. 1. The spectrum of the sample evacuated at 300–500 K, after the adsorption of hydrogen at 4 K, exhibits bands only at 4120 cm^{-1} and a less intense band at 4230 cm^{-1} which disappears on increasing the temperature up to 77 K. CO adsorption on this sample at 77 K leads to a band at 2145 cm^{-1} belonging to molecules bonded to the OH groups or non-specifically adsorbed on the surface /6/.

If the temperature of preliminary dehydration is increased to 600 K, the spectrum exhibits a new band of adsorbed H_2 at 4050 cm^{-1} accompanied by a less intense maximum at 4160 cm^{-1} . The two bands exist in the spectrum also at 77 K and disappear immediately after the removal of gaseous H_2 . When CO is adsorbed

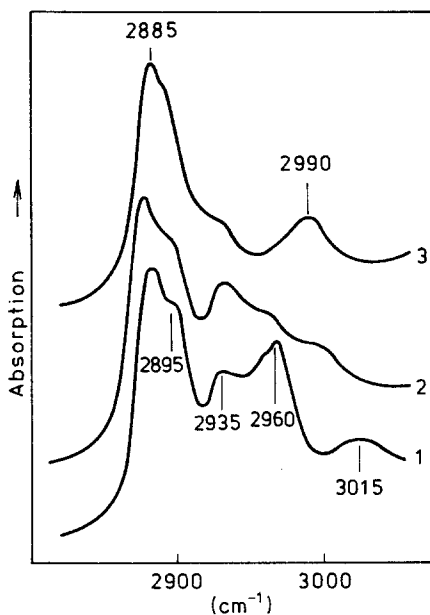


Fig. 2. Changes in the spectrum of adsorbed D_2 upon heating the ZnO sample from about 20 K (1) up to 50 (2) and 77 K (3)

on the sample pretreated under the same conditions absorption at about 2180 cm^{-1} is observed indicating the appearance of coordinatively unsaturated Zn atoms on the surface [6].

Studies of the adsorption of D_2 on ZnO evacuated at 723 K (Fig. 2) indicate that the spectrum of adsorbed dihydrogen is actually more complicated. Beside the bands at 2990 and 2885 cm^{-1} corresponding to those at 4160 and 4030 cm^{-1} in the H_2 spectrum, at least two additional bands are observed in the 2960 – 2935 cm^{-1} region at temperatures below 77 K. It means that between 4130 and 4080 cm^{-1} several overlapping bands exist that can be ascribed to the H_2 molecules bonded to the surface OH groups or non-specifically adsorbed on the oxide. More strongly bonded H_2 molecules absorb at 4160 and 4050 – 4030 cm^{-1} . The presence of a shoulder at 2895 cm^{-1} in the D_2 spectrum indicates that the low-frequency band consists of two unresolved peaks. The band at 4160 cm^{-1} , as well as the band at 4230 cm^{-1} of weakly bonded H_2 , like similar bands in the spectra of some other oxides [7], can be attributed to the combined frequency ν_{HH} and the low-frequency vibration of the molecule with respect to the surface.

For the appearance of the bands at 3500 and 1700 cm^{-1} belonging to the dissociatively adsorbed hydrogen, the sample should be evacuated at 623 K or higher,

and if the dehydration temperature is above 650 K, the intensity of the band at 1700 cm^{-1} seems to be higher than that of the bands of adsorbed dihydrogen, even though the band at 4050 cm^{-1} also grows significantly upon increasing the dehydration temperature (its maximum shifts to 4030 cm^{-1}). The bands of dissociatively adsorbed H_2 appear simultaneously with those of dihydrogen, even if the adsorption temperature is much lower than 77 K, thus indicating that the potential barrier of dissociation is very low. Temperature increase up to 77 or 300 K only slightly increases their intensity.

Changes in the spectrum of adsorbed CO accompanying the formation of centers for dissociative H_2 adsorption during heating in vacuum, are supported not only by the increased intensity of the coordinatively bonded CO bands, but also by certain qualitative variations. The spectrum becomes sensitive to surface coverage. At low coverages the spectrum exhibits a band at about 2180 cm^{-1} not removed by evacuation at 77 K. At higher pressures of CO it is replaced by a narrow intense band at 2167 cm^{-1} .

If hydrogen is added onto the sample with CO adsorbed at 77 K, no bands of adsorbed H_2 appear, and after cooling down to 4 K the spectrum exhibits an absorption band at 4120 cm^{-1} , just as in the case of a fully hydrated sample. It means that the sites of both dissociative and strong molecular adsorption of H_2 can be poisoned by CO. A prolonged evacuation at 77 K removes some of the coordinatively bonded CO, the band at 2167 cm^{-1} disappears, and the absorption at 2180 cm^{-1} restores its intensity. Further addition of H_2 shifted to 3520 and 1650 cm^{-1} . The bands of strongly bonded dehydrogen at 4030 and 4160 cm^{-1} arise only after the evacuation of the preadsorbed CO at temperatures higher than 77 K, when the absorption at 2180 cm^{-1} decreases. The addition of CO onto the sample with adsorbed hydrogen at 77 K leads to the immediate disappearance of the bands of dihydrogen and it shifts those of dissociatively adsorbed H_2 to 3520 and 1650 cm^{-1} like in Ref. /3/ at 300 K.

Thus, the bands of the dissociatively adsorbed hydrogen, as well as those of strongly bonded dihydrogen are present only in the spectra of the samples dehydrated at sufficiently high temperatures and do not appear after poisoning the adsorbent by coordinatively bonded CO molecules. This suggests that centers for both forms of adsorption include coordinatively unsaturated Zn atoms. Nevertheless, after dehydration at 600 K, molecular adsorption takes place, and after CO preadsorption the dissociative adsorption can be observed separately. Hence, the sites responsible for the strong molecular and dissociative adsorption of hydrogen on ZnO are not the same.

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