

## Infrared Study of ZnO Surface Properties

### I. Hydrogen and Deuterium Chemisorption at Room Temperature

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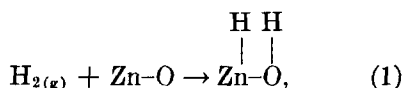
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Hydride and hydroxyl groups formed by reversible hydrogen chemisorption at room temperature give rise to bands which have escaped previous observation. Close examination of the coverage dependence of the Zn-H and O-H band frequencies reveals appreciable interaction between surface groups, which are regarded as confined in densely populated patches. Novel bands due to irreversibly adsorbed hydrogen, which are associated with bridged O-H...O and Zn-H-Zn structures, are also described. A dissociative chemisorption process is proposed.

#### INTRODUCTION

Hydrogen adsorption on ZnO is a quite involved process and has been the subject of many investigations (1-7). Several authors agree that both zinc and oxygen are involved, but the nature of the sites and the structure of the chemisorbed species are still debated. According to the more recent studies (8), carried out mainly by ir spectroscopy, at least two types of hydrogen chemisorption occur at room temperature. Type I is weak, fast, and reversible; type II is stronger, initially fast, and irreversible. Both occur without appreciable conductivity change.

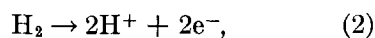
Type I chemisorption is characterized by two ir bands at 3498 and 1708 cm<sup>-1</sup> (9) which were assigned to the stretching vibrations of surface OH and ZnH groups formed according to the scheme:



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where the active Zn-O pairs were hypothesized as isolated or nearly isolated on the surface (10).

The quoted ir studies failed to find any adsorption characteristic of type II hydrogen. In order to explain this fact two structures for type II hydrogen have been proposed. In the first (9) the adsorbed hydrogen is supposed to be in a protonic form and formed following the reaction scheme:



where the protons are shared by three surface oxygen ions and the electrons produced are trapped in such a way that no conductivity change can take place. The second hypothesis (10) explains both the lack of ir bands and conductivity changes in terms of undissociated H<sub>2</sub> molecules trapped in octahedral cavities very near the surface.

Type I hydrogen is the active species for ethylene hydrogenation (10), while type II does not take part directly in the reaction.

It has also been suggested that the adsorbed amount, though quite small ( $\theta = 0.15$ ), might be confined in a few patches of small area where the concentration would be large (11).

Due to the disagreement on the nature of hydrogen adsorbed at room temperature, the overall subject was investigated in greater detail.

### EXPERIMENTAL

The catalyst was Kadox-25 zinc oxide (New Jersey Zinc Co.) prepared by combustion of zinc metal (BET surface area,  $10 \text{ m}^2/\text{g}$ ). About 0.3–0.4 g of the catalyst was compressed to form a pellet of 1-in. diameter at  $500 \text{ kg}/\text{cm}^2$ . The sample was inserted into a quartz cell supplied with getter ion and zeolite pumps. The ir spectra were recorded on a double-beam Perkin-Elmer 180 or a Beckman IR-7 spectrophotometer with a variable grating in the reference beam. The spectral slitwidths were  $8\text{--}5 \text{ cm}^{-1}$  and  $3\text{--}2 \text{ cm}^{-1}$  in the 4000- to 2500- and 1700- to  $750\text{-cm}^{-1}$  ranges, respectively. A standard thermal treatment was performed as follows. The sample was slowly heated to  $400^\circ\text{C}$  under a dynamic vacuum, then oxygen at 40-Torr pressure was admitted. After 5 min, the sample cell was outgassed until  $10^{-7}$  Torr was reached.

The oxygen admission and the successive evacuation were repeated three times, then the sample was cooled in oxygen and finally evacuated at room temperature down to  $10^{-7}$  Torr. By this procedure the surface carbonate complexes were mostly eliminated without loss of area or activity.

### RESULTS

The solid line of Fig. 1 is the spectrum of the sample after the standard thermal treatments. The weak bands in the 1600- to  $1200\text{-cm}^{-1}$  range, whose intensities slightly varies from sample to sample, are due to residual carbonate-like species which cannot be completely eliminated at the

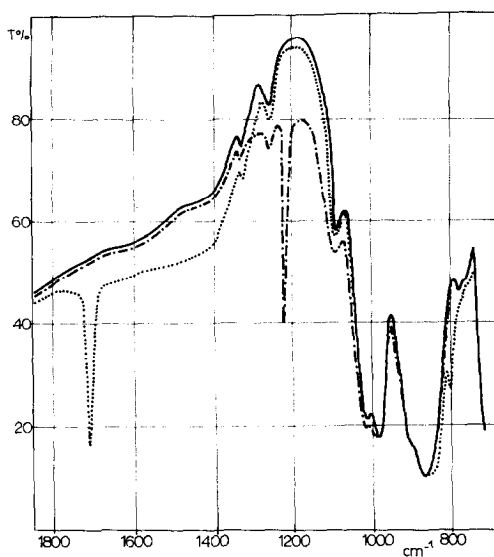


FIG. 1. Infrared spectrum of hydrogen and deuterium adsorbed on ZnO in the 1800- to  $900\text{-cm}^{-1}$  range (percentage transmission vs wavenumber). —, background; ····, in equilibrium with 100 Torr of  $\text{H}_2$ ; - - - -, in equilibrium with 100 Torr of  $\text{D}_2$ .

temperature of the standard treatment. The bands at 990 and  $870 \text{ cm}^{-1}$  are easily assigned to "bulk" multiphonon modes of crystalline ZnO (12). The dotted curve of Fig. 1 shows the effect of  $\text{H}_2$  adsorption ( $P = 100$  Torr; contact time, 15 min). Three new bands are present, at 1708 (strong and narrow), 1475 (very broad), and 817 (medium and narrow)  $\text{cm}^{-1}$ . A shoulder at  $850\text{--}45 \text{ cm}^{-1}$  is also observed. Moreover, in the following paragraphs it will be shown that the last two bands are superimposed on a weak and large absorption without an apparent maximum. The broken line of Fig. 1 illustrates the effect of  $\text{D}_2$  contact. A narrow band is observed at  $1233 \text{ cm}^{-1}$  which is superimposed on a larger one approximately centered at  $1075 \text{ cm}^{-1}$ . The pressure of 100 Torr was chosen because under these conditions the coverage of the reversible species is maximal and further pressure increases have no effect on the spectrum intensity. After 15 min the intensities of the large bands at  $1475 \text{ cm}^{-1}$

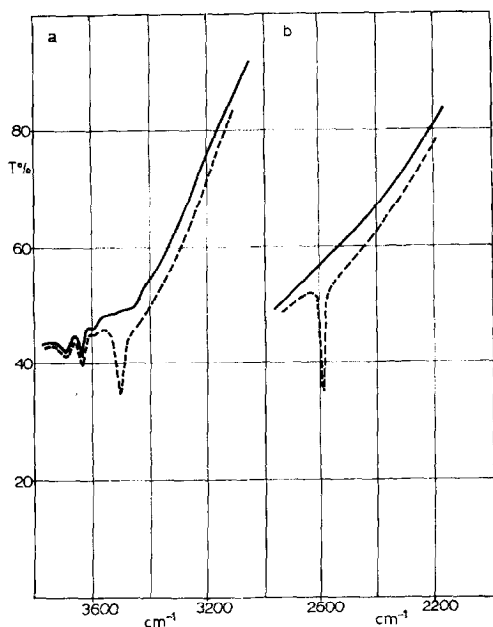


FIG. 2. Infrared spectrum of hydrogen and deuterium adsorbed on ZnO in the 3800- to 3000 (a)- and 2800- to 2000-cm<sup>-1</sup> ranges (b) (percentage transmission vs wavenumber). —, background; ---, in equilibrium with 100 Torr of H<sub>2</sub> and D<sub>2</sub>.

(H<sub>2</sub>-covered sample) and at 1075 cm<sup>-1</sup> (D<sub>2</sub>-covered sample) are still growing (although at a very low rate), and the maximum values are reached only after several hours. A mild evacuation at room temperature of the H<sub>2</sub>-covered samples eliminates the bands at 1708, 850-45, and 817 cm<sup>-1</sup>, leaving the large absorptions at 1475 cm<sup>-1</sup> practically unaffected; the same treatment on the D<sub>2</sub>-covered samples eliminates the narrow band at 1233 cm<sup>-1</sup> but does not affect the large absorption at ~1075 cm<sup>-1</sup>.

In the high-frequency region (2800-3800 cm<sup>-1</sup>) (Fig. 2a) the contact with hydrogen forms a narrow band at 3498 cm<sup>-1</sup> (which is destroyed upon a mild evacuation) and a large and very weak one approximately centered at 3400 cm<sup>-1</sup> (which is not removed by room temperature outgassing). The effect of deuterium (Fig. 2b) is to form a narrow band at 2585 cm<sup>-1</sup> (destroyed upon mild evacuation) and a large and very weak one approximately centered

at 2500 cm<sup>-1</sup> which is unaffected by room temperature outgassing. The bands at 3498 and 1708 cm<sup>-1</sup> (H<sub>2</sub>-treated samples) and at 2585 and 1233 cm<sup>-1</sup> (D<sub>2</sub>-treated samples) have already been observed (10), but all the others are reported for the first time. The data of Figs. 1 and 2 are summarized in Table 1.

Figures 3a and c show the behavior of the 3498- and 2585-cm<sup>-1</sup> bands upon decreasing the hydrogen and deuterium pressure. These bands are observed to decrease (in agreement with their reversible nature), while their frequencies move in a continuous way from the initial value (3498 and 2585 cm<sup>-1</sup>;  $P_{H_2} = P_{D_2} = 100$  Torr) to 3520 and 2598 cm<sup>-1</sup>, respectively.

In Figs. 3b and d the frequency of the two bands is plotted against their integrated intensities (assumed as a measure of the hydrogen coverage). In both cases a good linear relationship is observed, the overall shift being 22 and 15 cm<sup>-1</sup>, respectively.

Figures 4a and b show the effect of lowering the hydrogen and deuterium pressure on the 1708- and 1233-cm<sup>-1</sup> bands. In agreement with their reversible nature, their intensities decrease while their frequencies slightly move from the initial value (1708 and 1233 cm<sup>-1</sup>,  $P_{H_2} = P_{D_2} = 100$  Torr) to 1706 and 1231.5 cm<sup>-1</sup>, respectively.

Figure 5 shows the behavior of the 850- to 845- and 817-cm<sup>-1</sup> bands (characteristic of the H<sub>2</sub>-covered samples) upon decreasing the hydrogen pressure. The intensities decrease and the positions of the maximum shift to lower values. At the lowest coverages they are observed at 833-5 and at 815 cm<sup>-1</sup>, respectively ( $\Delta\nu = 10-17$  and 2 cm<sup>-1</sup>, respectively). The corresponding bands for the D<sub>2</sub>-treated samples are not observed, most probably because they fall in a spectral region where the sample is nearly opaque.

From Fig. 5 it can be clearly seen that, after complete desorption of the reversibly

TABLE 1  
Infrared Bands of H<sub>2</sub> and D<sub>2</sub> Adsorbed on ZnO

H <sub>2</sub>				D <sub>2</sub>				Isotopic ratios
$\nu$	$\Delta\nu_{\frac{1}{2}}$	Assignment		$\nu$	$\Delta\nu_{\frac{1}{2}}$	Assignment		
3498	29	$\nu$ (OH)	(I)	~2585	14.5	$\nu$ (OD)	(I)	1.34
~3400	300	$\nu$ (OH ... O)	(II)	2500	250	$\nu$ (OD ... O)	(II)	1.36
1708	12	$\nu$ (Zn-H)	(I)	1233	9	$\nu$ (Zn-D)	(I)	1.38
~1475	250	$\nu$ (ZnHZn)	(II)	~1075	200	$\nu$ (ZnDZn)	(II)	1.37
850-45	14.5	$\delta$ (OH)	(I)					
817	14.5	$\delta$ (Zn-H)	(I)					
~850-750	?	?	(II)					

adsorbed H<sub>2</sub>, the original background is not recovered in the 850- to 750-cm<sup>-1</sup> range. This can be explained either by hypothesizing the presence in the 850-750 region of a large band due to the hydrogen species irreversibly held (i.e., similar to those observed at ~3400 and ~1475 cm<sup>-1</sup>) or by assuming that a background variation due to a small sample conductivity change has

taken place. As a similar effect is not observed with D<sub>2</sub>-covered samples (for which the same conductivity change would be expected), we strongly favor the first hypothesis. If on an H<sub>2</sub>-covered sample ( $P_{H_2} = 100$  Torr), showing all the bands already described, D<sub>2</sub> gas is allowed to bleed in, the intensities of the bands due to reversibly adsorbed H<sub>2</sub> (3498, 1708, 850-45, and

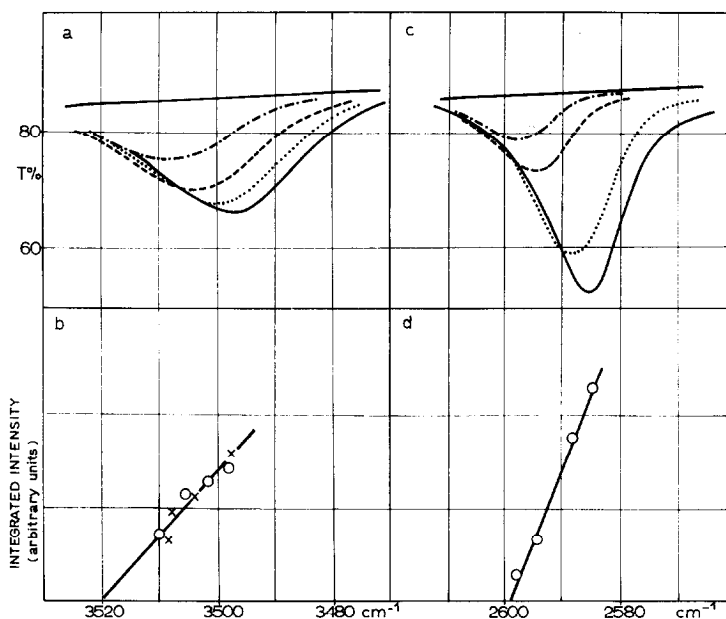


FIG. 3. (a) Dependence of the OH stretching band frequency and shape on coverage or pressure (transmission vs wavenumber). —, 100 Torr of H<sub>2</sub>, ····, 25 Torr of H<sub>2</sub>; ---, 5 Torr of H<sub>2</sub>; -·-·, 2 Torr of H<sub>2</sub>. (b) Plot of OH integrated intensity vs the peak position: O and X points refer to two different experiments. (c) Dependence of the OH stretching band frequency and shape on coverage or pressure (transmission vs wavenumber). The D<sub>2</sub> pressures are the same as in the former case. (d) Plot of the OD integrated intensity vs the peak position.

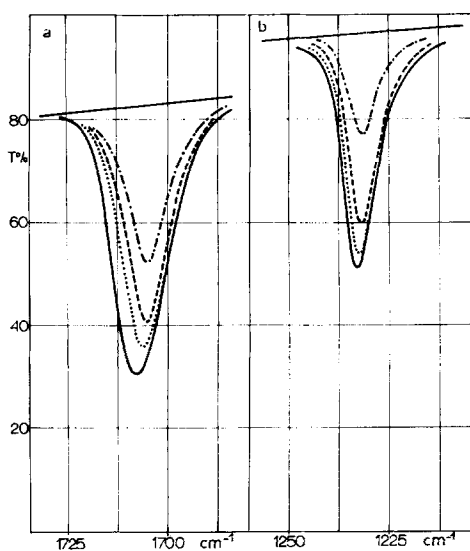


FIG. 4. Dependence of the frequency and shape of the Zn-H (a) and ZnD bands (b) on coverage or pressure. —, 100 Torr of H<sub>2</sub> (D<sub>2</sub>); ····, 25 Torr of H<sub>2</sub> (D<sub>2</sub>); ---, 4 Torr of H<sub>2</sub> (D<sub>2</sub>); - · - ·, 0.05 Torr of H<sub>2</sub> (D<sub>2</sub>).

817 cm<sup>-1</sup>) decrease, while those due to D<sub>2</sub> reversibly adsorbed increase. This means that the type I hydrogen quickly undergoes a displacement reaction, the extent of which depends on the H<sub>2</sub>-D<sub>2</sub> pressure ratio. At the same time the peak positions are unaffected with respect to fully H<sub>2</sub>- and D<sub>2</sub>-covered samples. The same experiment shows that the bands tentatively ascribed to irreversibly adsorbed hydrogen are unaffected either in position or in intensity by deuterium contact, in agreement with the well-known type II hydrogen behavior to isotopic exchange at room temperature (13, 14).

## DISCUSSION

### (a) Assignment of Type I Hydrogen Bands

As reported in Table 1, hydrogen and deuterium reversibly adsorbed at room temperature are associated with the following bands: 3498, 1708, 850-45, and 817 cm<sup>-1</sup> (hydrogen); and 2585 and 1233 cm<sup>-1</sup> (deuterium). The bands at 3498 and 1708

and at 2585 and 1233 cm<sup>-1</sup> have already been assigned to stretching modes of surface OH and Zn-H groups (H<sub>2</sub>) and of OD and Zn-D groups (D<sub>2</sub>) respectively, formed through reaction (1). As the bands observed at 850-45 and 817 cm<sup>-1</sup> on the H<sub>2</sub>-treated sample have the same pressure dependence as the 3498- and 1708-cm<sup>-1</sup> bands, we conclude that they are associated with the same surface groupings of atoms



formed by dissociative H<sub>2</sub> chemisorption on a zinc-oxygen pair (scheme 1); moreover, as they undergo the normal isotopic shift upon deuteration, we assign the 850- to 845- and 817-cm<sup>-1</sup> bands to  $\delta$  (OH) and  $\delta$  (Zn-H) modes, respectively, in agreement with the observation that the frequency of the first band is coverage sensitive (as is the O-H stretching) while the frequency of the second one is fairly insensitive (as is the Zn-H stretching). The proposed assignment is summarized in Table 1, where the observed isotopic ratios are also reported.

### (b) Assignment of Type II Hydrogen and Deuterium Bands

Hydrogen and deuterium irreversibly adsorbed on ZnO at room temperature are associated with the following bands: 3400 (very weak and broad), 1475 (medium and broad), 850-750 (very weak and broad), and 2500 (very weak and broad), and 1075 cm<sup>-1</sup> (medium and broad), respectively. The bands at 3400 and 1475 cm<sup>-1</sup> for the H<sub>2</sub>-covered samples fall on the low frequency side of the  $\nu$ (OH) and  $\nu$ (Zn-H) bands of reversible hydrogen. The same holds for D<sub>2</sub>-covered samples. Due to this remarkable correspondence, it is reasonable to assume that they are due to the same modes. *Irreversibly chemisorbed hydrogen is consequently dissociated on the surface.* The broadness of the bands due to OH, OD,

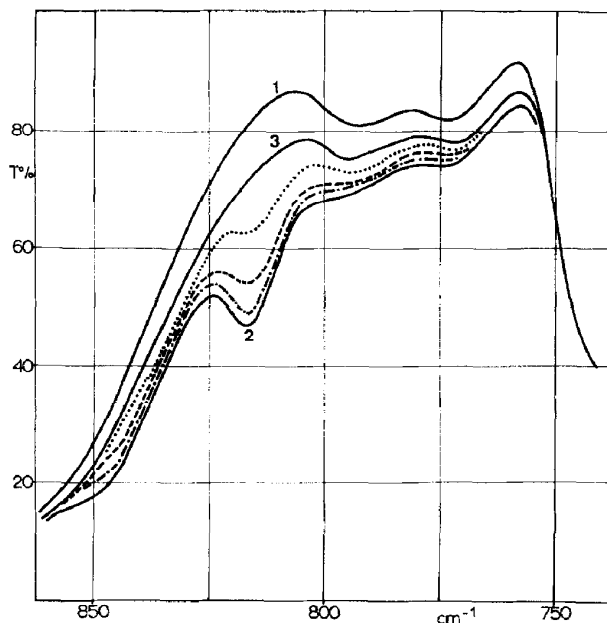
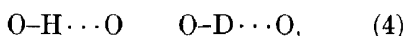


FIG. 5. Infrared spectrum of hydrogen adsorbed on ZnO in the 900- to 750-cm<sup>-1</sup> range (percentage transmission vs wavenumber). — (1), background; — (2), in equilibrium with 100 Torr of H<sub>2</sub>; ---, 40 Torr of H<sub>2</sub>; - - -, 10 Torr of H<sub>2</sub>; ····, 2 Torr of H<sub>2</sub>; and — (3), after outgassing at room temperature.

ZnH, and ZnD groups indicates that hydrogen-bonded and bridged structures are probably involved. For OH and OD groups the most probable structures are



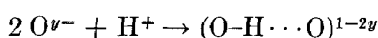
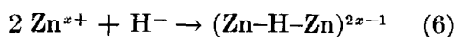
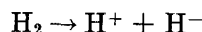
where the OH groups are hydrogen-bonded to adjacent oxygen ions. The small intensity and moderate frequency shift with respect to the free OH groups suggests a weak hydrogen bond in agreement with the large O-O distance in ZnO.

For the ZnH groups the following structure is proposed:



This assignment is in agreement with the literature data of homogeneous complexes containing hydrogen in a bridged position (13, 14). The proposed assignments are summarized in Table 1. In order to be stable, structure 5 needs two electrons in the Zn-H-Zn molecular orbital. As a consequence the dissociation mechanism

leading to both structures 4 and 5 can be schematized as follows:



The previous reaction scheme shows that in the irreversible hydrogen chemisorption four atoms (two zinc and two oxygen atoms) are involved. The adsorbing center is consequently more complex with respect to that involved in type I hydrogen chemisorption. The "bridged" nature of type II hydrogen, implying extended interaction of the hydrogen atoms with more than one oxygen and zinc ion, seems to confirm the hypothesis (15) that this type of hydrogen is located in subsurface cavities.

#### (c) Coverage Dependence of the OH and Zn-H Frequencies of Type I Hydrogen

The frequencies of the bands associated with surface OH and OD groups are

strongly influenced by coverage. This can be explained in several ways, such as surface heterogeneity, dipole-dipole interaction, or induced heterogeneity. The first hypothesis is not consistent with our data. In fact, if OH groups on different sites were involved (with stretching and bending frequencies ranging from 3520 to 3498  $\text{cm}^{-1}$  and from 850–45 to 833  $\text{cm}^{-1}$ , respectively) the shape of the bands would be expected to change in desorption, because different groups disappear at different rate.<sup>2</sup> Moreover, the resulting shape modification does not involve any band crossing. Quite to the contrary, the experimental data show a fairly constant shape and band crossing. Such behavior could well be explained in terms of dipole-dipole interaction between OH groups suitably aligned on a regular surface, as both theoretical and experimental work has shown (16). The continuous frequency change with coverage is explained in terms of a physical modification of the ir band nature, which is gradually changing with coverage, from a collective mode involving several parallel oscillators ( $\vartheta = 1$ ) to a localized one characteristic of isolated groups ( $\vartheta = 0$ ). This attractive hypothesis must be discarded because it is in conflict with the data obtained by partial isotopic exchange. In fact, random substitution of the OH groups absorbing at 3498  $\text{cm}^{-1}$  by OD absorbing at 2585  $\text{cm}^{-1}$  should drastically change the OH-OH and OD-OD coupling, OH-OD coupling being negligible due to the large frequency difference. As a consequence, the OH and OD frequencies should be expected to be dependent on the extent of isotopic exchange. The reported experiment shows on the contrary that, at constant maximum coverage ( $\text{H}_2 + \text{D}_2$ ), the OH and OD bands are located at the position characteristic of fully hydrogenated or deuterated samples and do not vary

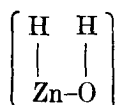
<sup>2</sup> Some surface heterogeneity is not excluded, as the shape of the Zn-H and O-H band is slightly asymmetric.

with the extent of isotopic exchange. Induced heterogeneity is the most likely factor to be invoked, i.e., each molecule interacting with the surface exerts a physical influence on the preadsorbed ones leading to a continuous modification of the spectroscopic properties.

Two possibilities can be envisaged: Either the physical influence is transmitted without damping through the solid to distant molecules (collective effect), or it dies away within a limited number of Zn-O spacings (long-range effect). In the first case the Zn-O active pairs can be isolated centers while in the second they must be confined into densely populated areas. The collective effect could be due to free electrons populating the conduction band. However, after the standard pretreatment in oxygen, the ZnO conduction band is empty and  $\text{H}_2$  adsorption does not contribute to populating it, as no appreciable conductivity and ir transparency changes have been observed with room-temperature  $\text{H}_2$  chemisorption. The lack of formation of interstitial Zn or  $\text{Zn}^+$  atoms as a consequence of room-temperature  $\text{H}_2$  adsorption is also demonstrated by the absence of any effect due to oxygen in the gas phase, which is known to interact with interstitial donor centers and to restore the initial insulating character. The induced heterogeneity is consequently due to "long-range effects" and, as a consequence, the reversible OH groups are confined to densely populated patches.

In homogeneous compounds containing OH groups, the  $\nu(\text{OH})$  and  $\delta(\text{OH})$  frequencies respond to charge variations induced on the oxygen and hydrogen atoms by "field" and " $\sigma$ -inductive" effects caused by different substituents. In particular, if the overall effect leads to an increase of the bond polarity, the net result is a rise in the  $\nu(\text{OH})$  and a lowering of the  $\delta(\text{OH})$  frequency. The opposite trend is observed if the OH polarity is lowered leading to more covalent OH bonds (17). In a completely

similar way, the frequencies of the OH groups of a partially ionic oxidic surface should respond to changes of the local Madelung fields and to “ $\sigma$ -inductive effect” variations along the Zn–O bonds. As a consequence, because on the surface the  $\nu(\text{OH})$  frequency decreases and the  $\delta(\text{OH})$  frequency increases with increasing coverage, it is concluded that the interaction between



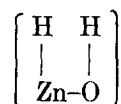
groupings within the densely populated patches leads to a continuous decrease of the OH bond polarity.

The frequency value of the Zn–H stretching mode is consistent, as in homogeneous zinc hydrides, with a high covalent character, the residual polarity being ascribed to a small negative charge on the hydrogen atom (18, 19). With respect to the OH stretching, the dependence on coverage of the Zn–H frequency is much less pronounced in absolute value and goes in the opposite direction ( $\Delta\nu = +2 \text{ cm}^{-1}$  as against  $\Delta\nu = -22 \text{ cm}^{-1}$ ). The small shift value is not surprising if the different response of the X–H stretching frequencies to field and  $\sigma$ -inductive effects is taken into account (17). For instance, when X is a first row element (such as oxygen), the (X–H) frequency is very responsive, while for X belonging to different rows it is less responsive or it can behave in the opposite way. The latter situation is found when the X–H bond (as in our case) is polarized with a negative charge on the hydrogen atom (17). Due to this fact, the increase of the (Zn–H) frequency with coverage is again an indication of an increase in covalency.

#### (d) *The Nature of the Adsorbing Patches*

From the previous discussion the conclusion has been reached that adjacent Zn–H and OH dipoles are oriented in

opposite ways and that every polarity increase (and/or decrease) in one of the bonds is accompanied by the same effect on the other. Another conclusion is that the



pairs in the patches are interacting in such a way that every increase in their concentrations is accompanied by a definite decrease in the bond polarity. As collective effects deriving from electronic properties of the solid were discarded, the problem of the nature and of the maximum distance at which the “long-range effects” are effective on the surface (and hence of the extension and structure of the adsorbing patches) is still open.

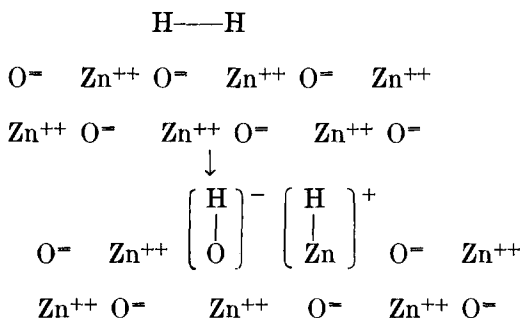
The problem of estimating the relative contributions to the “long-range effects” of the coulombic and  $\sigma$ -inductive (polarization along the Zn–O bonds) forces is, at the moment, a formidable barrier (20), the situation being exceedingly complicated by the fact that ZnO is intermediate between a purely ionic and a purely covalent solid. Nevertheless, a few considerations can be given. On ionic solid surfaces, the ions suffer a reduced Madelung potential, the reduction with respect to the bulk being larger on high-index faces (21). However, this is not the only effect which is important on the ionic or partly ionic surfaces, as polarization must be taken into account. In solid ionic compounds, polarization is known to be more extensive the lower the coordination number and depends on both the polarizing power and the polarizability of the ions. Both of these are enhanced by low coordinative situations (22). Surface ions are in a lower coordinative state with respect to the bulk: As a consequence, on the surface, polarization is expected to be enhanced to an extent that is larger on high-index faces.

On an ideal purely ionic surface, polarization leads to a distortion of the elec-



tronic charge density of the ions. On the partly covalent solid ZnO, polarization increases the covalency of the Zn-O bonds. In conclusion, a decrease of the surface Madelung potential and an increase of polarization are the two main interrelated effects which must be taken into account on the ionic or partly ionic surfaces.

Chemisorption is a process leading to an increase or to a decrease of the Madelung energy. Hence chemisorption is invariably accompanied by an increase or a decrease in surface covalence. Hydrogen chemisorption on ZnO is an example of process leading to a decrease of the Madelung energy. This can be easily shown in the following (completely ionic) model:

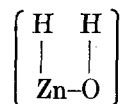


where oxygen and zinc ions are replaced by covalent hydride and hydroxyl groups carrying a reduced charge. Coulombic forces (and hence the interrelated polarization effects) appreciably extend to several Zn-O spacings: As a consequence the replacement of the original pair with a ZnH-OH one is followed by a perturbation extended to a large area, leading to a decrease of the local Madelung field. If in this area another ZnH-OH pair is present it will respond by increasing the covalent character of the bonds, as has been experimentally proved.

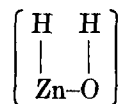
The observed effect agrees with the well-known behavior of the frequency of adsorbed CO on varying the local field strength, as investigated by Hush and Williams (23).

As far as the linear dependence of the

stretching band on

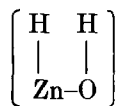


population is concerned, it can be explained only if the following conditions are satisfied: (a) fairly uniform density of

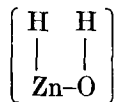


groups within the patches at all coverages; and (b) additivity of the spectroscopic effects caused at a given site by the surrounding groups. The first point implies that the active Zn-O sites for hydrogen chemisorption within the patches are equivalent or nearly equivalent from the energetic point of view, in agreement with the previous observation that the surface heterogeneity does not play an important role in the type I hydrogen chemisorption.

The



groups at the patch boundaries should be in a less covalent situation with respect to those located in more internal positions, as they are under the influence of only half the



neighbor groups. As a consequence, the frequencies of the external Zn-H and OH groups, are expected to occur at lower and higher values, respectively, so justifying the presence of distinct tails on the lower and higher frequency sides of the Zn-H and O-H bands, respectively. As the tail intensity is not negligible, it is inferred that the patch dimensions are not very large. Precise figures, however, cannot be given, because the average distance of the interacting groupings is not known.

The band frequency of the Zn-H-Zn groups of irreversible chemisorbed hydrogen (type II) does not appreciably change with the type I hydrogen coverage. This observation seems to imply that the sites for type I and type II hydrogen adsorption are mutually independent and hence located at distant positions. However, due to the broad nature of the Zn-H-Zn band, small frequency shifts can easily escape experimental observation. As a consequence, the presence of both type I and type II hydrogen in the same patches cannot be ruled out completely.

#### CONCLUSIONS

From the investigation of H<sub>2</sub> chemisorption on ZnO at room temperature the following facts have been established:

(i) Zn-H and O-H groups of reversibly adsorbed hydrogen (type I) have ir-active bending frequencies at 817 and 850-45 cm<sup>-1</sup>, respectively.

(ii) The active sites for type I hydrogen are confined into densely populated patches.

(iii) Zn-H and O-H groups of type I hydrogen strongly interact via "long-range" effects and as a consequence the corresponding stretching and bending frequencies change continuously with the coverage.

(iv) Type II hydrogen is in a dissociated form, the hydrogen atoms being bridged between neighboring oxygen and zinc ions.

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