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Configurational Effects in the Adsorption of HD on ZnO

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Washington, DC 20234

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(HD) adsorption on ZnO surfaces has ~~been studied by~~ infrared spectroscopy as a function of ZnO temperature. It is shown that at 300K, the configuration Zn(H)-O(D) is preferred, as expected on thermodynamic grounds. As the temperature is lowered, the configuration Zn(D)-O(H) becomes preferred on kinetic grounds. We demonstrate that configuration reversal on heating must proceed via HD desorption and subsequent re-adsorption. This behavior is consistent with a model in which the transition state ~~for HD adsorption is charac~~terized by nearly complete dissociation of the H-D bond.

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Configurational Effects in the Adsorption of HD on ZnO

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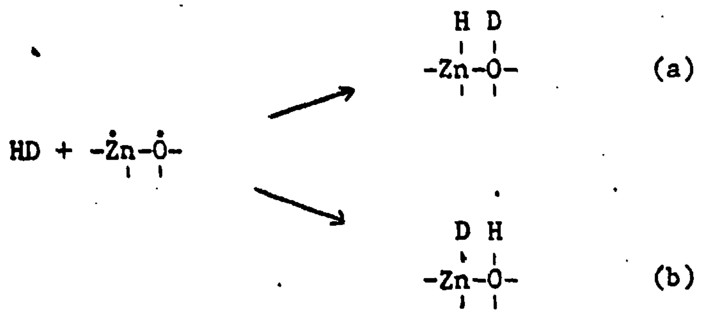
Abstract

HD adsorption on ZnO surfaces has been studied by infrared spectroscopy as a function of ZnO temperature. It is shown that at 300K, the configuration Zn(H)-O(D) is preferred, as expected on thermodynamic grounds. As the temperature is lowered, the configuration Zn(D)-O(H) becomes preferred on kinetic grounds. We demonstrate that configuration reversal on heating must proceed via HD desorption and subsequent re-adsorption. This behavior is consistent with a model in which the transition state for HD adsorption is characterized by nearly complete dissociation of the H-D bond.

Kinetic isotope effects have long been recognized as a powerful tool for obtaining experimental information about reaction mechanisms and energy pathways. In many instances, measured isotope effects are used to confirm (or deny) the rate-determining nature of a particular step in a complex reaction sequence. Therefore, it is particularly interesting to find examples of elementary reactions which show an isotope effect, since such simple experimental results can provide reliable checks for theoretical calculations of reaction dynamics.

The dissociative adsorption of HD on ZnO provides such an example. A decade ago, using infrared spectroscopy, Kokes et al. (1) reported that the HD molecule can be adsorbed in two possible configurations:



$$\mathrm{HD} + -\overset{\bullet}{\underset{|}{\mathrm{Zn}}}-\overset{\bullet}{\underset{|}{\mathrm{O}}}- \begin{array}{l} \nearrow \; -\overset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{Zn}}}}-\overset{\mathrm{D}}{\overset{|}{\underset{|}{\mathrm{O}}}}- \quad (a) \\ \searrow \; -\overset{\mathrm{D}}{\overset{|}{\underset{|}{\mathrm{Zn}}}}-\overset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{O}}}}- \quad (b) \end{array} \qquad (1)$$

For convenience, we shall refer to configurations (a) and (b) as $(HD)_a$ and $(DH)_a$, respectively.

At room temperature, when the adsorbate layer was in equilibrium with a gas phase H_2:HD:D_2 mixture (also equilibrated), Kokes observed that the configuration $(HD)_a$ was favored over $(DH)_a$ by a factor of 3:1. This preference was attributed to different equilibrium adsorption energies for the two configurations, arising from differences in the zero point vibrational energies of species (a) and (b) above. Kokes found that the observed $(HD)_a$:$(DH)_a$ ratio of 3:1 agreed well with the predicted ratio based on zero-point energy differences, calculated using the observed stretching frequencies and reasonable assumptions for the bending frequencies.

However, when HD gas was admitted to the ZnO surface at 78 K, Kokes observed that the preference was reversed: the observed $(HD)_a$:$(DH)_a$ ratio was 1:20! Since the HD adsorption process shown by Eq. (1) is irreversible at 78 K (1,2), the low temperature result reflects a difference between the kinetic barriers for adsorption into the two configurations. To explain this difference within the format of activated complex theory, Kokes proposed: 1) that the OH (or OD) stretching mode corresponded to the reaction coordinate for the adsorption process, and 2) that the position of the transition state on the potential energy surface was characterized by nearly complete dissociation of the H-D bond, as illustrated schematically in Fig. 2. The barrier height difference was therefore primarily due to the zero point energy difference between the ZnH and ZnD vibrational modes; this difference was consistent with the observed kinetic preference for $(DH)_a$ vs. $(HD)_a$ at 78 K.

The assumption that the OH (or OD) stretching mode is the reaction coordinate can only be verified by a theoretical analysis of the potential energy surface. Similarly, the overall accuracy of activated complex theory for this reaction must be determined by theoretical calculations. However, the assumption that the transition state is characterized by nearly complete dissociation of the H-D bond can be examined experimentally. In this note, we describe such an experiment.

A ZnO sample is prepared and mounted in the sample cell for IR spectroscopy, as described previously (2). The sample is then cooled to 88 K, and HD gas is admitted to the cell. When adsorption ceases, the remaining HD gas is evacuated, and the adsorbate concentrations n_{ZnH}, n_{OD}, n_{ZnD}, and n_{OH} are determined from the integrated intensities of the respective vibrational bands (3). Within the accuracy of the intensity vs. coverage calibration (± 10%), we observe $n_{ZnH} = n_{OD}$ and $n_{ZnD} = n_{OH}$, as expected if $(HD)_a$ and $(DH)_a$ are the only adsorbate configurations. The ratio $(HD)_a$:$(DH)_a$ is calculated as $(n_{ZnH} + n_{OD})/(n_{ZnD} + n_{OH})$.

The initial ratio observed following adsorption at 88 K, is $(DH)_a:(HD)_a = 9:1$. While this is smaller than the value obtained at 78 K by Kokes, it does confirm the existence of the kinetic isotope effect.

We then allow the sample to warm gradually (1 K/min), while constantly pumping on the cell. The adsorbate coverages are recorded at ~30 K intervals. The results are shown in Fig. 1, which gives the adsorbate concentrations (μmole/gm ZnO) as a function of warm-up temperature. We observe that all of the concentrations decrease monotonically, corresponding to desorption of HD molecules. In particular, there is no tendency for the $(DH)_a:(HD)_a$ ratio to change as the temperature is increased.

In contrast, Kokes had observed an increase in the $(HD)_a:(DH)_a$ ratio as a similarly prepared surface was warmed in 80 torr of HD. As we have shown elsewhere (2), H_2 desorption commences below 170 K. Therefore, we can conclude that the tendency toward $(DH)_a \rightarrow (HD)_a$ configuration reversal observed by Kokes was due to desorption followed by readsorption. Since the kinetic isotope effect is less pronounced at higher temperature, the $(DH)_a:(HD)_a$ preference decreased for subsequently re-adsorbing molecules, and hence the observed $(DH)_a:(HD)_a$ ratio on the surface appeared to tend toward reversal in Kokes' studies.

Our results in Fig. 1 demonstrate that in the absence of gas phase re-adsorption, there is no tendency for configuration reversal on the surface. In other words, an HD molecule must desorb and then re-adsorb in order to change its configuration. This strongly supports Kokes' second assumption, that the transition state is characterized by nearly complete dissociation of the H-D bond. Rotation prior to desorption would only be expected if the H-D bond integrity is developed on the pre-desorption side of the reaction coordinate; this is not the case for desorption of H_2 from ZnO.

This concept is shown schematically in Fig. 2, which indicates the potential surfaces for HD and DH adsorption based on our results. These surfaces include the zero-point vibrational energy contributions. We stress that the figure is intended to illustrate the comparative differences between the adsorption pathways leading to $(HD)_a$ and $(DH)_a$; the absolute values of the barrier heights and the adsorption energies are obtained from our measured values of these quantitites for H_2 adsorption (2), after correction for estimated zero point energy differences between $(H_2)_a$, $(HD)_a$ and $(DH)_a$. The key features are that the activation barrier leading to $(HD)_a$ is larger than the barrier to $(DH)_a$ by about 135 cm^{-1} (= 390 cal/mole), while the adsorption energy for $(HD)_a$ is greater than for $(DH)_a$ by about 230 cm^{-1} (= 660 cal/mole). The activation barrier difference is based on our observed kinetic $(HD)_a$:$(DH)_a$ ratio at 88 K, and corresponds to the assumption that all of the effect is due to zero-point energy effects in the transition state. The adsorption energy difference is based on the room temperature ratio of $(HD)_a$:$(DH)_a$ = 3:1, which we experimentally verified.

In summary, we have confirmed both the equilibrium and kinetic isotope effects reported by Kokes (1), and have demonstrated the new result that HD molecules must desorb and re-adsorb in order to reverse their configuration. In addition, we believe that these interesting phenomena for the HD/ZnO system, which have now been confirmed experimentally in two laboratories, can provide a reliable model system for evaluating the accuracy of theoretical descriptions of reaction dynamics involving surface processes.

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References

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3. G. L. Griffin and J. T. Yates, Jr., (Submitted for publication).

Figure Captions

Figure 1 Concentration of $(DH)_a$ species (n_{ZnH} and n_{OH}) and $(HD)_a$ species (n_{ZnH} and n_{OD}) during warm-up *in vacuo* of ZnO exposed to HD at 88 K.

Figure 2 Potential energy surface for adsorption processes $HD(g) \rightarrow (HD)_a$ and $HD(g) \rightarrow (DH)_a$.

Adsorbate Composition During Desorption of HD from ZnO

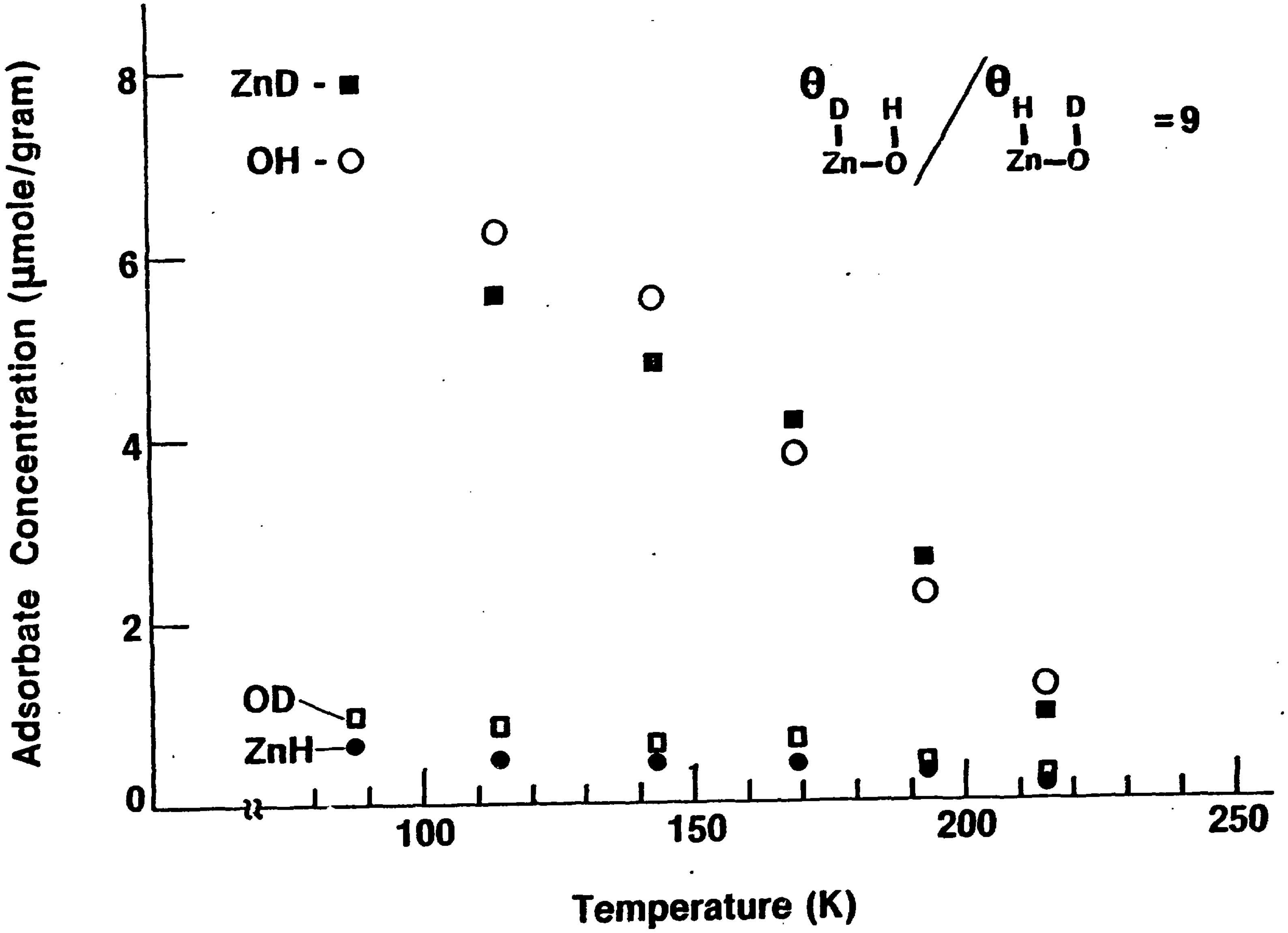

Figure 1

Energetics of 'HD' vs 'DH' Adsorption on ZnO

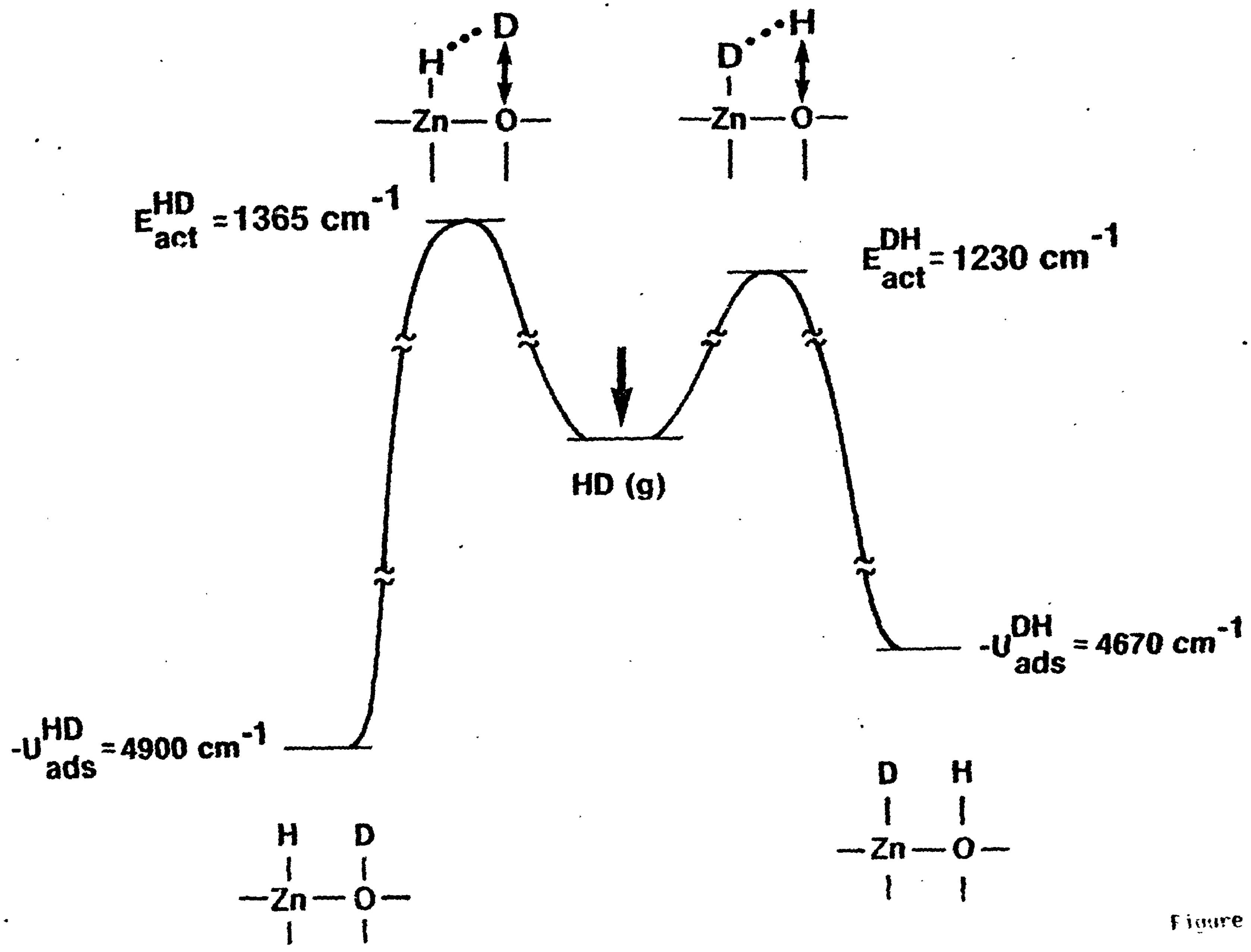

Figure 2