

Surface Diffusion of Hydrogen and Oxygen on Tungsten

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V-Centers in Evaporated Alkali Halide Films*

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(Received November 3, 1955)

It has been shown by other workers that *F*-centers can be formed in thin films of the alkali halides by simultaneous evaporation of the alkali halide and an alkali metal.¹ As the following data will show, it is also possible to form *V*-centers in thin alkali halide films by an analogous process in which the alkali halide and a halogen are simultaneously evaporated onto a quartz substrate held at low temperature. A preliminary study of these films has shown that the *V*-centers so formed are independent of the halogen used and depend only on the alkali halide.

Figure 1 shows the results for KI. Curve 1 gives the optical density of a thin film formed by the simultaneous evaporation of KI and I₂ onto a quartz substrate at -183°C. The absorption measurements in this and all the following cases were made at -183°C. Curve 2 gives the optical density of a film formed by the evaporation of KI and Br₂ onto a quartz substrate at -183°C. The third curve, taken from the work of Uchida and Makai,² gives the optical density of a large single crystal of KI colored by heating in I₂ vapor. The absorption of this crystal was measured at room temperature. The similarity between these curves is striking.

Similar results have been obtained for KBr. Figure 2, curves 1 and 2, show the optical density of thin films of KBr formed at -183°C by simultaneous evaporation with Br₂ and I₂ respectively. Absorption measurements were made at -183°C. It is to be noted that the absorption bands again do not depend upon the halogen used and that they differ markedly from the bands formed in KI. Curve 3, Fig. 2, shows the optical density of a large single crystal of KBr x-rayed at -140°C and measured at -180°C

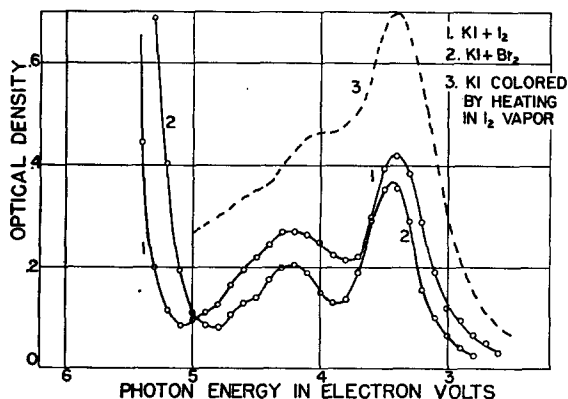


FIG. 1. *V*-centers in thin films of KI. See text for explanation of curves.

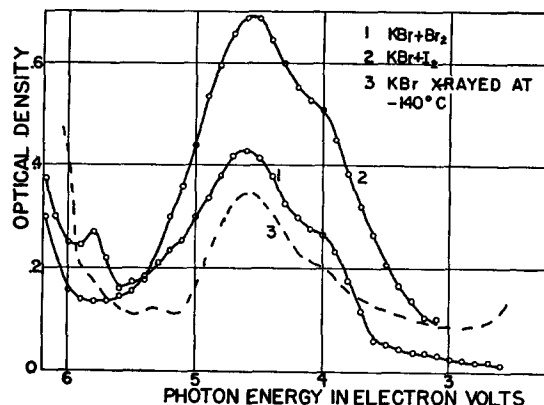


FIG. 2. *V*-centers in thin films of KBr. See text for explanation of curves.

by Dorendorf.³ He identifies the band structure shown with a combination of the *V*₂, *V*₄, and *V*₇ bands.

Since the thickness of the films discussed above varied from about 300 Å to 600 Å, a rough calculation indicates that the density of color centers was about 10²⁰/cm³.

In connection with the KBr data it should be pointed out that no KI fundamental absorption peak occurs in the KBr plus I₂ films. This demonstrates that the number of I⁻ ions introduced into the KBr lattice during the evaporation was less than about one part in a hundred. The bands are thus characteristic of the KBr lattice in spite of the large density of color centers.

We consider the foregoing data to be strong evidence in support of the Seitz vacancy models of the *V*-centers.⁴

A more complete report on the above and similar work will be made in the near future.

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¹ R. Kaiser, *Z. Physik* **132**, 482 (1952).

² Y. Uchida and Y. Nakai, *J. Phys. Soc. Japan* **9**, 928 (1954).

³ H. Dorendorf, *Z. Physik* **129**, 317 (1951).

⁴ F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

Surface Diffusion of Hydrogen and Oxygen on Tungsten*

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(Received November 4, 1955)

FIELD emission studies of the surface migration of hydrogen and oxygen on tungsten at low and very high coverages have been reported previously.^{1,2} Slow activated diffusion occurs in the former case while spreading with a sharp boundary, moving almost uniformly over the tip, occurs for very high coverage with both gases.

This note describes the behavior observed when 1 monolayer is initially deposited on the covered portion of a 011 oriented tungsten tip. Under these conditions migration sets in at 205°K with hydrogen and 500°K with oxygen. The diffusion is of the moving boundary type, but differs from the low temperature, high coverage case in that the boundary spreads radially outward from the 011 face. The first visible change consists of a darkening of the zone connecting the central 011 face with the $\bar{1}21$ face (nearest the covered portion of the tip). Slow motion pictures show that contamination of the $\bar{1}21$, $\bar{1}12$, and $\bar{1}\bar{1}2$ faces and their vicinals occurs before the moving boundary reaches them; i.e., adsorbate races ahead of the boundary on the zones connecting these faces with the central 011 face. Circular boundaries with $\bar{1}10$ and $10\bar{1}$ at their centers are also observed and eventually merge with the

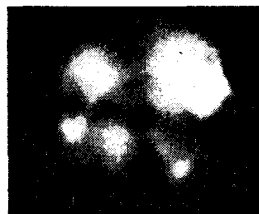


FIG. 1. Radial boundary diffusion of hydrogen on a 011 oriented tungsten field emission point at 220°K.

central boundary. The latter moves at rates of ~ 25 Å/sec. Figure 1, taken from a motion picture film, shows radial spreading of hydrogen in progress.

The following mechanism seems to explain these observations. In b.c.c. metals the 011 faces are the most closely packed, i.e., smoothest. Zones like 011– $\bar{1}21$ – $\bar{1}10$ are largely made up of terraces of 011. It is probable that ad-atoms are most weakly held and most mobile on the smoothest faces. Thus the zone $\bar{1}10$ – $\bar{1}21$ –011 constitutes a low impedance channel over which adsorbate flows from the covered portion into the central 011 face. Migration over this face is rapid and ad-atoms spill over the edges, into the regions of the tip which are atomically rough. These contain many high-energy sites, which will trap ad-atoms and hold them immobile. However, once the "traps" have been saturated, migration can occur even on the rough portions of the tip at rates comparable to those on 011. This is tantamount to diffusion with precipitation and accounts for the sharp moving boundary.

Preliminary estimates of the activation energies of the process, based on spreading rates and jump frequencies of $10^{12}e^{-E/kT}$ show that $E \sim 9$ kcal for hydrogen and ~ 19 kcal for oxygen. This is considerably lower than the values of 16 and 30 kcal, respectively, found at coverages of ~ 0.1 monolayer. The latter undoubtedly correspond to movement from high-energy ("trap") sites, since these will be very incompletely filled at this coverage. It is interesting that Müller has recently reported a value of 16 kcal for the activation energy of the oxygen on tungsten diffusion at high coverage,³ in reasonable agreement with our value.

These findings show that two types of surface heterogeneity are active in decreasing heats of adsorption with increasing coverage on metal surfaces: 1. Crystallographic anisotropy. 2. The existence of inherently different adsorption sites on a given face.

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¹ R. Gomer and R. Wortman, *J. Chem. Phys.* **23**, 1741 (1955).

² R. Gomer, *Advances in Catalysis VII* (Academic Press, Inc., New York, 1955); R. Gomer and J. K. Hulm, *J. Am. Chem. Soc.* **75**, 4114 (1953).

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Rotation-Resisting Energy Barrier in the Nitric Acid Molecule

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(Received October 3, 1955)

PALM and Kilpatrick have recently computed the barrier height in nitric acid¹ with the aid of our spectroscopic data, but without mentioning that we reported similar calculations, along with the spectroscopic observations.² We used four variations of method, and obtained results in the range 8.4–10.2 kcal/mole (mean 9.4 kcal/mole). They used five variations and obtained results 8.3–10.5 kcal/mole (mean 9.7 kcal/mole).³ Thus the rounded figure 9–10 kcal/mole is confirmed by the new, independent calculation. We have commented previously² on the physical nature of this somewhat large potential.

* Deceased.

¹ A. Palm and M. Kilpatrick, *J. Chem. Phys.* **23**, 1562 (1955).

² Cohn, Ingold, and Poole, *J. Chem. Soc.* 4272 (1952).

³ They give an additional decimal place, which, however, has no significance.

On the Use of Local Symmetry in Analyzing the Infrared Spectra of Complex Molecules

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RECENT infrared spectra of binuclear metal carbonyls,^{1,2} have been explained by a method using local symmetry. This note presents a description of the method.

The validity of the method of local symmetry depends on assuming that a molecule can be resolved into relatively noninteracting vibrating units (the units chosen being those of highest symmetry); and that, therefore, the selection rules for the isolated units are valid for those not isolated. Also, if a molecule contains several similar clusters of atoms, these will give rise to vibrations having the same frequency. For molecules of high symmetry these assumptions yield results identical with those of an exact treatment.

The method of local symmetry is also useful in predicting the spectra of systems with slightly perturbed local symmetry, such as is exhibited by the carbon monoxide ligand systems in $C_5H_5 \times (CO)_n \times C_5H_5$.¹ This is best illustrated by a calculation on the before-mentioned compounds, assuming these have the structures proposed by G. Wilkinson.¹⁻³ The infrared spectra of these compounds show that their pseudo rings *cannot* be planar. However, a *perturbed* planar ring will explain the spectra.¹

Let the unperturbed problem be an n -membered ($n=4,5$) carbon monoxide ring system of symmetry D_{nh} . If r_r represents the C–O stretching coordinate of the r th carbon monoxide ligand, the C–O stretching symmetry coordinates are⁴

$$S_l = n^{-1/2} \sum_{r=0}^{n-1} (\omega^l)^r r_r, \quad \omega = i^{2\pi/n} \quad (1)$$

Upon inversion, Eq. (1) becomes

$$\eta_r = n^{-1/2} \sum_{l=0}^{n-1} (\omega^{-r})^l S_l \quad (2)$$

For the slightly interacting carbon monoxide ligands composing the cyclic system, we can set the normal coordinates Q_l equal to $\mu^{1/2} S_l$, μ being the reduced mass of a carbon monoxide group.

To the first order, the puckering of the carbon monoxide ring system does not change the normal coordinates, Q_l . This is reasonable since the ligands are very weakly bonded together in the ring.² Since we know the normal coordinates Q_l and can compute the instantaneous dipole moment of the carbon monoxide stretching modes, we can calculate the relative intensities of the vibrational modes Q_l .

Using a model in which the carbon atoms of the carbon monoxide ring system lie in a common plane together with the oxygen atom numbered 0, and in which the oxygens numbered 1 to $n-1$ are directed alternately above and below this plane at equal inclinations α , we find the following expressions for the dipole moment \mathbf{M} (g is the charge associated with each atom of a given ligand):

$$\mathbf{M} = g \cos \alpha (\eta_1 - \eta_3) \mathbf{i} + g (\eta_0 - \eta_2 \cos \alpha) \mathbf{j} + g \sin \alpha (\eta_1 + \eta_3 - \eta_2) \mathbf{k}, \quad n=4.$$

$$\mathbf{M} = g \cos \alpha \left(\cos \frac{\pi}{10} (\eta_1 - \eta_1) + \cos \frac{3\pi}{10} (\eta_3 - \eta_2) \right) \mathbf{i} + g \left(\eta_0 + \cos \alpha \left[\sin \frac{\pi}{10} (\eta_1 + \eta_1) - \sin \frac{3\pi}{10} (\eta_2 + \eta_3) \right] \right) \mathbf{j} + g \sin \alpha (\eta_1 - \eta_2 + \eta_3 - \eta_4) \mathbf{k}, \quad n=5. \quad (3)$$

Since

$$\frac{\partial \mathbf{M}}{\partial Q_l} = \sum_{r=0}^{n-1} \frac{\partial \mathbf{M}}{\partial r_r} \frac{\partial r_r}{\partial Q_l}, \quad (4)$$

we can, by using (2) and (3), calculate the variation of the dipole moment with respect to the normal coordinates Q_l . Such a cal-