**INFRARED STUDIES OF THE
ADSORPTION-DESORPTION OF WATER ON
MONOCLINIC AND TETRAGONAL ZrO_2 AS
A FUNCTION OF TEMPERATURE**

P. A. Agron, E. L. Fuller, H. F. Holmes

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SEPTEMBER 1974

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ABSTRACT

The adsorption-desorption cycling studies at elevated temperatures of submonolayer water coverages on the surface of two zirconium oxide polymorphs leads to a partial resolution of the vibrational frequencies due to chemisorbed and physisorbed species. The narrow stretching frequency band, $\nu(O_1-H)_M$ for the monoclinic phase ZrO_2-G , at 3760 cm^{-1} is assigned to chemisorbed OH groups bound to a single cation at crystal corners and edges. This singly coordinated anion is here designated as a "free" hydroxyl anion. This orientation enables the anion to accept an H-bonding donor water molecule. The polarizing effect of the H-bond lowers the stretch frequency of this hydroxyl anion. The relatively narrow band $\nu(O_2-H)_M$ at 3660 cm^{-1} is assigned to chemisorbed hydroxyls coordinated to more than a single cation on oxide lattice sites of low index faces. In this instance the oxygen atom of the latter anion is sterically unable to accept an H-bonding donor water molecule.

The partially resolved high frequency bands $\nu(O_{1a}-H)_T$ and $\nu(O_{1b}-H)_T$ at 3740 and 3720 cm^{-1} , respectively, are attributed to chemically bound "free" hydroxyl groups of the tetragonal oxide, ZrO_2-C , at two non-equivalent oxygen lattice sites. The stretching frequencies of these two species are likewise lowered by H-bonded water. Hydroxyls coordinated to more than one cation, at two different lattice spacings, are assigned to $\nu(O_{2a}-H)_T = 3662\text{ cm}^{-1}$ and $\nu(O_{2b}-H)_T = 3645\text{ cm}^{-1}$. At 300°C the half width

of the "free" hydroxyl is $\sim 70 \text{ cm}^{-1}$ and $\sim 95 \text{ cm}^{-1}$ for the hydroxyls coordinated to multiple cations.

The partially resolved broader bands, of several hundred wave numbers, observed at the lower frequencies on extensive desorption from both polymorphs are attributed to water molecules strongly bound to the oxide surface (Table I, 2). The energy and extent of the H-bonded network of water molecules held on the surface or in micropores of these two polymorphic oxides may be judged from the position and intensity of the bending frequency, respectively, for the water molecule.

The resolution of the H_2O sub-bands is accomplished by exchange reactions with D_2O . The corresponding $\nu(\text{O-D})$ stretch bands are observed. The ratios of the assigned $\nu(\text{O-H})/\nu(\text{O-D})$ stretch frequencies show satisfactory agreement with the theoretical ratio. The rapid exchange of isotopic species indicates that the exchange takes place on the solid surfaces. The extent of D_2O exchange is governed by the number of successive adsorption-desorption cycles.

INTRODUCTION

The physical and chemical adsorption of water vapor on high surface area zirconium oxide has received emphasis here^(1, 2) because of its importance as a ceramic and catalytic oxide. De Boer and his associates⁽³⁾ utilized gas adsorption isotherms in earlier studies to characterize the nature of zirconia prepared under varying conditions. An extensive report on the preparation, physical properties and catalytic behavior of this oxide appeared recently⁽⁴⁾

Early x-ray studies^(5,6) identified the existence of the tetragonal and monoclinic phases of ZrO_2 . Accurate structural determinations of monoclinic single crystals of ZrO_2 have been reported.^(7,8) The structure of the primitive tetragonal cell was derived from a high temperature x-ray diffraction study.⁽⁹⁾

Differential thermal analysis^(4,10) of precipitated amorphous zirconia, under alkaline conditions, indicates that a crystallization to the metastable tetragonal form takes place at 405°C. Refluxing the precipitate in neutral or acid media yields the monoclinic oxide.⁽⁴⁾ The latter is transformed to the tetragonal phase above 1200°C. On cooling the inversion to the stable monoclinic form takes place at a transition point ~150°C lower. This hysteresis has been observed by several investigators.^(4,10) Various proposed mechanisms have been made for the sluggish transformation^(7,8) and for the large metastable region observed for the tetragonal phase at the lower temperatures.^(1,11)

Recent calorimetric measurements of the heats of immersion⁽¹⁾ in water of outgassed samples of ZrO_2 have shown that the initial interaction of water with the oxide surface is chemical in nature. The character of the subsequent slow heat release appears to be complex. The degree of chemisorption and slow heat release has varied with the method of preparation^(1,2) and with the specific polymorphic phase studied. Gas adsorption isotherms of one of the samples used in this study has been reported.⁽²⁾

The structural nature of water plays a dominant role in its chemical and physical properties. A comprehensive treatise on the physics and physical chemistry of water has appeared recently.^(12a) Coulson^(12b) proposed that the dipole moment of the water molecule is due to the lone-pair electrons occupying the sp^3 orbitals. Hydrogen bonds directed toward

these lone pairs lead to tetrahedrally coordinated polymers of water in the condensed phase. X-ray⁽¹³⁾ and neutron⁽¹⁴⁾ diffraction, infrared⁽¹⁵⁾ and Raman⁽¹⁶⁾ spectroscopic studies of water have been instructive in testing the proposed configurations which best fit the observed experimental data. These studies yield a time average measure of the possible conformations in the liquid phase.

Infrared⁽¹⁵⁾ and Raman⁽¹⁶⁾ studies of H_2O - D_2O mixtures have led to the suggestion that the broad stretching O-H water frequency (3200-3600 cm^{-1}) is composed of 4 gaussian contour bands and is attributed to different polymeric, H-bonded species. The lowering of the water stretch frequency on hydrogen bonding is a reflection of a lowered O-H force constant.⁽¹⁷⁾ Hydrogen bonding here also leads to a large increase in the absorption coefficient of the stretching frequency.⁽¹⁸⁾ On the other hand, the bending mode of the water molecule appears in the 1600 to 1650 cm^{-1} region. For the latter mode, shifts to the higher frequency occur when H-bonded networks form, but the absorption coefficient is not altered to any large extent.⁽¹⁸⁾ Thus, this bending mode also serves as an additional indication of the extent of H-bonded molecular water adsorbed on the oxide.

Several investigators^(15,16,18) propose that the broadened $\nu(O-H)$ for the water stretch band is due to the superposition of contributions from H-bonded multimeric species. Sheppard suggests⁽¹⁷⁾ that this comes about from the anharmonic coupling of $\nu(O-H) \pm n\nu'(O-H...O)$ where $\nu'(O-H...O)$ is of the order of 100 to 200 cm^{-1} . Fermi resonance between $\nu(O-H)$ and combination bands which are of similar frequency and the same symmetry class as the fundamental may also contribute to this effect. However, the latter appears to be less likely in the frozen matrix study or when water is adsorbed on high surface area solids.

Matrix freezing of hydrogen bonded molecules at varying dilutions of the inert matrix media has been used for analyzing infrared spectra.⁽¹⁹⁾ The study of water molecules isolated in low temperature matrices were reported for the stretching and bending frequencies for the monomer, dimer and multimer species of H-bonded water molecules. An infrared study of the matrix isolated molecules of H₂O, D₂O and HDO has appeared more recently.⁽²⁰⁾ The vibrational frequencies of the H₂O species observed as a function of matrix dilution are in good agreement in both investigations. The values observed for the bending frequencies⁽²⁰⁾ range from 1597 cm⁻¹ to 1633 cm⁻¹. The lower value is assigned to the H₂O monomer, and the higher frequencies are attributed to H-bonded polymers. The analogous bending frequencies of water adsorbed on the zirconium oxide surfaces are pertinent to this study and will be taken up again in the discussion.

EXPERIMENTAL

A double-beam Beckman IR-12 filter-grating spectrophotometer, modified⁽¹²⁾ to encompass a high temperature sample cell mounted in a "stretch" compartment and incorporated into the optical bench, was used for this study. A PbS photoconducting detector, at liquid nitrogen temperature, served to cover the range from 2400 to 4000 cm⁻¹ with a reproducibly high sensitivity. The lower frequency spectral range utilized a thermocouple with the appropriate electronics.

Three hundred milligrams of each of the two zirconium oxide powders were pressed in a 13/16-in.-diam die with a force of 40,800 psi.⁽²¹⁾ This results in a packing density of 22.5 mg/cm². The pressed discs were

stored in covered petri dishes over an extended period prior to this study.

All of the reported spectra were obtained at indicated equilibrium sample temperatures ranging from 40 to 500°. In this investigation the exposure to water vapor was limited to a maximum of 4.6 torr in the attempt to resolve the spectral bands observed in adsorption studies of water on similar oxides. (4, 21) The scans reported here were acquired for each set of conditions after equilibrating at respective temperatures for periods of at least 16 hours. Outgassing pressures were in the range of 10^{-5} to 10^{-6} torr. Most spectra were acquired at scanning rates of 3.2 to 8 $\text{cm}^{-1}/\text{min}$. Faster scans were taken to observe the rate of change and to delineate the approach to steady state. The spectral data are presented in chronological sequence to aid in the correlation and interpretation of the observed effects. A fixed scale expansion, achieved by reference beam attenuation, was used throughout each of the two studies.

The infrared technique was selected to follow the nature of the adsorption-desorption of water on a sample of both the monoclinic and tetragonal preparations with a previous history of analysis. The $\text{ZrO}_2\text{-G}$ sample, primarily monoclinic phase, has been characterized by nitrogen adsorption (2) to have a surface area of $23.7 \text{ m}^2/\text{g}$. The heats of immersion (1) have also been reported for the selected tetragonal preparation, $\text{ZrO}_2\text{-C}$, with a surface area of $52.7 \text{ m}^2/\text{g}$. It was hoped that the infrared study of repeated adsorption-desorption cycling of water at selected temperatures would point up the differences in surface chemistry for the two polymorphic forms of ZrO_2 .

The regions of $2400\text{--}4000\text{ cm}^{-1}$ and the $1400\text{--}1300\text{ cm}^{-1}$ spectral scans were examined extensively for the $\text{ZrO}_2\text{-G}$ wafer to delineate the vibrational stretching and bending modes, respectively, of the adsorbed water molecule. The lower region was omitted for the $\text{ZrO}_2\text{-C}$ wafer because, in this instance, it showed a great deal of opacity. A 200-mg $\text{ZrO}_2\text{-C}$ pressed wafer showed that the transmission in the bending region was analogous to that in the $\text{ZrO}_2\text{-G}$ disc and was omitted from this study. It is generally acknowledged that the vibrational frequency contributions of molecular bound water on high surface area solids lie in a broad band from 2400 to 3600 cm^{-1} .⁽²²⁾ The unresolved broad band of adsorbed water on oxide surfaces has been associated with H-bonded polynuclear water molecules.^(22,23) In desorption studies, narrow bands appearing at higher frequencies have been assigned to the stretching vibration frequency of isolated OH groups bound to one or more cations.^(22,23)

$\text{ZrO}_2\text{-G}$: ADSORPTION-DESORPTION STUDIES

Figure 1. Transmission Spectra, $2400\text{--}4000\text{ cm}^{-1}$, at 40 and 100°C

The initial spectra of the $\text{ZrO}_2\text{-G}$ wafer gave a broad unresolved transmission band in the stretching frequency region of molecular water. On extensive outgassing at 40°C the trace (1a) indicates the initial removal of weakly bound water molecules in the lower frequency region and at the same time yields a narrow sideband at 3760 cm^{-1} . Several cycles of outgassing and exposure at 40°C to 4.6 torr of water vapor results in trace (1b); wherein, the frequency peak at 3760 cm^{-1} is no longer resolved. A subsequent outgassing of the disc at 100°C is shown in (1c). On a four-fold expanded frequency scale, from 3600 to 4000 cm^{-1} , the partially resolved

Fig. 1. Transmission Spectra, $2400\text{--}4000\text{ cm}^{-1}$

Region, Adsorption-Desorption of H_2O on $\text{ZrO}_2\text{-G}$, at 40 and 100°C .

1a Initial outgassing of sample at 40°C .

1a' Same, on a four-fold expanded frequency scale.

1b Adsorption of H_2O at 4.6 torr and 40°C .

1c Outgassed sample at 100°C after several repeated cycles of (1a) and (1b)

1c' Same, on a four-fold expanded scale, $3600\text{--}4000\text{ cm}^{-1}$

shoulder of the 100°C trace (1c') shows a lower concentration of the 3760 cm^{-1} specie than that observed for the initial outgassing (1a').

Figure 2. Transmission Spectra, 2400-4000 cm^{-1} , at 40, 200, and 300°C

The trace, (2b), obtained on exposure to 4.6 torr H_2O at 200°C indicates a lower concentration of molecular bound water compared to that observed at the same pressure in (2a) at 40°C. In the high frequency region a poorly resolved shoulder in the region of 3760 cm^{-1} is shown on the expanded scale in (2b') for the 200°C isotherm. The transmission spectra in (2c) and in the expanded scale (2c') are obtained on outgassing at 200°C. Here, the increased resolution of the high frequency shoulder is accompanied by a depopulation of the species contributing to the lower frequency region. The spectral peaks in the 2860 to 3000 cm^{-1} region are due to C-H stretch frequency bands. The adsorption of traces of organic species occurs from back diffusion and degradation products from stopcock grease.* A subsequent exposure of the sample to 1 atm of oxygen at 300°C for an extended period results in a large reduction of this band. A more effective removal of this organic deposit is accomplished at higher temperature treatments.⁽²⁴⁾ The reduction in the spectral intensities at the lower frequencies under vacuum at 300°C (2d) indicates the further removal of the less firmly bound water. At this point the faint resolution of an absorbance peak at 3660 cm^{-1} emerges in (2d) and 2d').

Figure 3. Transmission Spectra, 2400-4000 cm^{-1} , at 400 and 500°C

The resulting spectra on exposure to 4.6 torr H_2O at 400°C is given in (3a). Outgassing at 400°C and 500°C results in the traces shown in (3b) and 3c), respectively. Here the monotonic reduction in absorbance

*Apiezon N Stopcock grease used for stopcocks of vacuum manifold.

Fig. 2. Transmission Spectra, 2400-4000 cm^{-1}

Region, Adsorption-Desorption of H_2O on $\text{ZrO}_2\text{-G}$ at 40, 200 and 300°C.

2a Adsorption of H_2O at 4.6 torr and 40°C

2b Adsorption of H_2O at 4.6 torr and 200°C

2b' Same, on a four-fold expanded frequency scale, 3600-4000 cm^{-1}

2c Outgassed sample at 200°C

2c' Same, on a four-fold expanded frequency scale, 3600-4000 cm^{-1}

2d Outgassed sample at 300°C

2d' Same, on a four-fold expanded scale, 3600-4000 cm^{-1}

Fig. 3. Transmission Spectra, $2400-4000 \text{ cm}^{-1}$

Region, Adsorption-Desorption of H_2O on $\text{ZrO}_2\text{-G}$ at 400 and 500°C .

3a Adsorption of H_2O at 4.6 torr and 400°C

3b Outgassed sample at 400°C

3b' Same, on a four-fold expanded scale, $3600-4000 \text{ cm}^{-1}$

3c Outgassed sample at 500°C

3c' Same, on a four-fold expanded scale, $3600-4000 \text{ cm}^{-1}$

3d' Adsorption of H_2O at 4.6 torr and 500°C

of the lower spectral frequencies on desorption is accompanied by a progressively sharper resolution of the band at 3660 cm^{-1} . The decreases in the populations of the two high-frequency stretch vibrations, of the sample outgassed at 400 and 500°C , are shown in (3b') and (3c'), respectively. The oxide has been equilibrated with 4.6 torr H_2O at 500°C in (3d'), for comparative spectra.

Figure 4. Absorbance Spectra, $3100\text{--}4000\text{ cm}^{-1}$, at 500 , 300 and 100°C

The absorbance spectrum on outgassing at 500°C is shown in (4a) over the frequency region from 3100 to 4000 cm^{-1} . A two-fold shift of the absorbance scale is inserted at (4a'). The spectra obtained on subsequent cooling of the system under vacuum to 300°C , (4b) and (4b'), and then to 100°C , (4c) and (4c'), indicated a progressive improvement in the resolution of several bands. The emergence of the 3760 cm^{-1} band is accompanied by an improved resolution of the 3660 cm^{-1} band.

Figure 5. Transmission Spectra, $3200\text{--}4000\text{ cm}^{-1}$, at 500 , 300 , 100 and 40°C

Figure 5 shows the transmission spectra on a four-fold expanded frequency scale at the same desorption conditions observed in Fig. 4. On reducing the temperature of the outgassed sample (5a) from 500°C to 300°C , a coincidence occurs in the intensity of the band at 3660 cm^{-1} . The trace at 300°C (5b) is therefore displaced for a better visual comparison with the spectra of (5a). Cooling further under vacuum to 100 and 40°C resulted in almost identical spectra (5c), for these two temperatures, over the measured range of frequency. The latter trace shows better resolution of the bands at 3760 cm^{-1} and 3660 cm^{-1} with additional improvements in the resolution of the much broader sub-bands at 3580 cm^{-1} and 3480 cm^{-1} . The assignments are listed in Table 1.

Fig. 4. Absorbance Spectra, 3100-4000 cm⁻¹ Region,

of H₂O on ZrO₂-G at 500, 300 and 100°C

4a Outgassed sample at 500°C

4a' Same, on 2-fold expanded absorbance scale

4b Sample cooled under vacuum to 300°C

4b' Same, on 2-fold expanded absorbance scale

4c Sample cooled under vacuum to 100°C

4c' Same, on 2-fold expanded absorbance scale.

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Fig. 5. Transmission Spectra, 3200-4000 cm^{-1}

(on a four-fold expanded frequency scale) at 500, 300, 100 and 40°C

5a Outgassed sample at 500°C

5b Sample cooled under vacuum to 300°C

5c Sample cooled under vacuum to 100°C

Figure 6. Transmission Spectra, H_2O - D_2O Exchange, 2400 - 4000 cm^{-1} , at 40°C

After outgassing the sample at 500°C and cooling under vacuum to 40°C , the transmission spectrum resulted in (6a). This trace shows no marked difference from that obtained on a previous cooling cycle from 500°C under vacuum. The extensive outgassing here represents an unsaturated state where additional water species can be chemically as well as physically adsorbed. An initial exposure of the system at 40°C to $200\text{ }\mu\text{ D}_2\text{O}$ drops rapidly to a pressure of $45\text{ }\mu$ on adsorption. The resulting transmission spectrum is shown in (6b). Outgassing the sample at 40°C results in the trace shown in (6c). Here the frequency peak at 2770 cm^{-1} is the O-D analog of the O-H stretch at 3760 cm^{-1} , and likewise, the peak at 2695 cm^{-1} is the equivalent vibrational mode observed for the O-H mode at 3660 cm^{-1} . Additional exposure to $4\text{ torr D}_2\text{O}$ leads to the unresolved broad H_2O and D_2O bands shown in (6d).

Figure 7. H_2O and D_2O Desorption-Adsorption Spectra at 300°C

The sample equilibrated with $4\text{ torr D}_2\text{O}$ (6d) was outgassed at 300°C . The resulting spectrum is shown in (7a). Here the resolution of the 3660 cm^{-1} band and the related band at 2695 cm^{-1} is increased because of the reduction in population of the associated lower stretching frequency species. On further exposure to $4\text{ torr D}_2\text{O}$ at 300°C (7b), the resulting increase in the population of the low frequency species is not sufficient to obliterate the 3660 cm^{-1} and 2695 cm^{-1} bands. A repeated outgassing of the sample leads to the spectrum shown in (7c). Each of the above traces is displaced to more clearly show the development of the absorption bands of both the bound H_2O and D_2O regions. The successive exchange of

Fig. 6. Transmission Spectra of D_2O Exchange on ZrO_2-G , $2400-4000\text{ cm}^{-1}$ Region at 40°C .

- 6a Sample reduced to 40°C in vacuum, following extended desorption of H_2O at 500°C
- 6b Exchange of D_2O at $200\text{ }\mu$
- 6c Outgassed sample at 10^{-5} torr
- 6d Exchange at 4 torr D_2O

Fig. 7. Adsorption-Desorption of H₂O-D₂O Exchange Species on ZrO₂-G at 300°C.

- 7a Desorption of H₂O-D₂O species at 300°C
- 7b Exchange of 4 torr D₂O at 300°C
- 7c Repeated desorption of H₂O-D₂O species at 300°C

D₂O at 300°C, followed by outgassing, adds effectively to the further delineation of the sub-bands of the water stretching frequencies at 3580 and 3480 cm⁻¹. A correlation of the corresponding stretch frequencies of the water sub-bands and of the O-H and O-D species is given in Table 1.

Figure 8. Bending Region for H₂O Molecule, 1450-1800 cm⁻¹, at 40°C

The frequency region of 1600-1650 cm⁻¹ has been associated with the bending frequency of molecular water. The lower wave number has been attributed to mono-molecular water and the higher values have been assigned to "polymeric" H-bonded water.⁽¹⁹⁾ Figure 8 presents the effect of step-wise adsorption of water at 40°C on exposure to a dehydrated sample. The transmission spectrum of (8a) was obtained after the oxide had been outgassed at 500°C and allowed to cool under vacuum to 40°C. The spectrum of this extensively desorbed sample suggests that the partially resolved peak at 1595 cm⁻¹ is due to the bending motion of uni-molecular water.⁽¹⁹⁾ As the surface is exposed to a larger partial pressure of water, the resulting band broadens, increases in the integrated absorbance and shifts toward the higher frequencies of 1620 cm⁻¹ at 100 μ H₂O (8b), and to 1640 cm⁻¹ at 2.7 torr H₂O (8c). The peak at 1540 cm⁻¹ does not change markedly with observed experimental conditions and is assumed to represent a vibration contribution from the zirconium oxide lattice. The spectrum (8d) is obtained on exposure to water at 4.6 torr. The increased absorbance of the peak at 1640 cm⁻¹ is indicative of a further increase in the concentration of multimolecular water bound to the oxide. Steps in the desorption of water at 40°C are shown in the following traces. The successive outgassing of the oxide at 5 × 10⁻² and 10⁻⁵ torr (8e, 8f) causes the

Fig. 8. Transmission Spectra of the Bending

Region of H_2O Adsorbed on $\text{ZrO}_2\text{-G}$, $1450\text{-}1800\text{ cm}^{-1}$ Region, at 40°C .

- 8a Temperature reduced to 40°C , under vacuum, after outgassing at 500°C
- 8b Adsorption of H_2O at 100 μ pressure
- 8c Adsorption of molecular water at 2.6 torr H_2O
- 8d Adsorption of molecular water at 4.6 torr H_2O
- 8e Spectral trace on reduction of water pressure to 50 μ
- 8f Outgassed sample at 10^{-5} torr.

bending frequency band to shift toward 1600 cm^{-1} , indicating a decrease in the population of H-bonded molecular water species.

Figure 9. Bending Frequency Region for H_2O , $1450\text{--}1800\text{ cm}^{-1}$, at 300 and 500°C

Traces in Fig. 9 show the spectral shift accompanying desorption from the oxide after equilibrating with 4.6 torr H_2O at 300°C (9a). The progressive outgassing of the sample at $1\text{ }\mu$ and 10^{-5} torr at 300°C, followed by 10^{-5} at 500°C, is displayed in (9b), (9c), and (9d), respectively. The intensity of the water spectra can be judged relative to the ZrO_2 lattice vibration at 1540 cm^{-1} . Here each of the spectral traces has been shifted by 0.15 units in the transmittance scale to give a better visual estimate of the decrease in intensity and the displacement of the bending frequency mode as a function of the desorption conditions. Here again the progressive outgassing at 300°C reduces the broad peak at 1600 cm^{-1} to a narrower band at 1590 cm^{-1} and to an unresolved shoulder of the 1540 cm^{-1} band at 500°C. It should be noted that the trace of (9c) was reproducible before and after exposure to 4.6 torr of water.

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Fig. 9. Transmission Spectra of the Bending Region

of H_2O Adsorbed on $\text{ZrO}_2\text{-G}$, $1450\text{-}1800 \text{ cm}^{-1}$ Region, at 300 and 500°C .

9a Adsorption of molecular water at 4 torr H_2O at 300°C

9b Outgassed sample at 1μ and 300°C

9c Outgassed sample at 10^{-5} torr and 300°C

9d Desorbed sample at 10^{-5} torr and 500°C

Table 1. Stretch Vibration Frequencies of
Monoclinic $\text{ZrO}_2\text{-G}$

Spectral Species		$\nu(\text{O-H})$	$\nu(\text{O-D})$
Schematic Representation	Band Type	(cm^{-1})	(cm^{-1})
$\text{Zr}-(\text{O}_1-\text{H})^{(a)}$	$\nu(\text{O}_1-\text{H})_{\text{M}}^{(a)}$	3760	2770
$\text{Zr} > (\text{O}_2-\text{H})^{(b)}$	$\nu(\text{O}_2-\text{H})_{\text{M}}^{(b)}$	3660	2695
G_2	Bound H_2O	3580	2640
G_3	Bound H_2O	3480	2560

(a) Frequency contribution of surface O-H groups bound to single cation ("free" hydroxyl group) of the monoclinic phase.

(b) Stretch frequency of bound O-H groups coordinated to more than a single cation.

ZrO₂-C: ADSORPTION-DESORPTION STUDIESFigure 10. Transmission Spectra, 2400-4000 cm⁻¹, at and 200°C

The transmission spectrum of the expanded 3600-4000 cm⁻¹ region (10a') again reveals a sharply resolved band at 3760 cm⁻¹ on the initial outgassing of the sample at 100°C. Exposure to 4.6 torr H₂O at this temperature gives rise to a broad absorption band, (10b), eliminating the resolution of the 3760 cm⁻¹ band. Subsequent outgassing at 100°C results in (10c), a trace similar to the initial outgassing. The difference is observed in (10c') where the intensity of the resolved 3760 cm⁻¹ band is reduced somewhat. A further outgassing at 200°C results in trace (10d) and (10d'). The buildup of the band due to organic matter in the 2850-3000 cm⁻¹ region is again encountered and was removed at a later stage by exposure to O₂ at 300 and 400°C.

Figure 11. Transmission Spectra, 2400-4000 cm⁻¹, at 300°C

Outgassing the sample at 300°C resulted in trace (11a) and (11a'). The expanded trace (11a') indicates a broad shoulder extending from 3720 to 3760 cm⁻¹. Exposure to 4.6 torr H₂O, (11b), results in an increased absorbance in the lower frequency region and a reduced resolution of the high frequency shoulder as noted in (11b) and (11b'). A subsequent outgassing depopulates the low frequency region (11c) and also changes the resolution and contribution of the high frequency species (11c').

Fig. 10. Transmission Spectra, 2400-4000 cm⁻¹

Region, of ZrO₂-C at 100 and 200°C.

10a' Initial outgassing of sample at 100°C, 3600-4000 cm⁻¹ region, on 4-fold expanded frequency scale.

10b Adsorption of water at 4.6 torr, 2400-4000 cm⁻¹, at 100°C

10c Desorption of sample at 100°C, 2400-4000 cm⁻¹ region.

10c' Same, on a 4-fold expanded frequency scale, 3600-4000 cm⁻¹ region

10d Desorption of water at 200°C, 2400-4000 cm⁻¹ region.

10d' Same, on a 4-fold expanded frequency scale, 3600-4000 cm⁻¹

Fig. 11. Transmission Spectra, $2400\text{--}400\text{ cm}^{-1}$
Region, of $\text{ZrO}_2\text{-C}$, at 300°C .

11a Outgassed sample.

11a' Same, on a 4-fold expanded frequency scale, $3600\text{--}4000\text{ cm}^{-1}$
region.

11b Adsorption of H_2O at 4.6 torr, $2400\text{--}4000\text{ cm}^{-1}$ region.

11b' Same, on a 4-fold expanded frequency scale, $3600\text{--}4000\text{ cm}^{-1}$
region.

11c Desorption of water, $2400\text{--}4000\text{ cm}^{-1}$ region.

11c' Same, on a 4-fold expanded frequency scale, $3600\text{--}4000\text{ cm}^{-1}$
region.

Figure 12. Transmission Spectra as a Function of Temperature

Trace (W) and (W') represent the spectra obtained in an earlier exposure to 4.6 torr H_2O at $100^\circ C$ and gives some measure of the extent of desorption as a function of temperature. On outgassing at $400^\circ C$ a large depopulation in the low frequency region is observed in (12a). A short exposure of the sample to 100 torr O_2 followed by outgassing at $400^\circ C$, (12b), removes the organic band (G) and at the same time raises the transmittance in the 3700 to 4000 cm^{-1} region by a factor of about 2.

The expanded trace (12b') indicates that partial resolution of the high frequency band has shifted toward 3725 cm^{-1} and a band at 3660 cm^{-1} becomes visible. Spectral traces (12c) and (12c') are obtained on reducing the temperature to 300° under vacuum. Here an improved resolution of broad sub-bands appear at the 3595 cm^{-1} and at the 3440 cm^{-1} wavenumbers. The band at 3725 cm^{-1} shows better resolution in (12d) and (12d') on proceeding to an outgassing temperature of $500^\circ C$.

Figure 13. Absorbance Spectra, 3000 - 4000 cm^{-1} , 400 , 500 and $300^\circ C$ (1st cycle)

The absorbance spectrum obtained at an outgassing temperature of $400^\circ C$ is given in (13a), showing the partial resolution of bands at 3725 , 3660 , and 3440 cm^{-1} . Outgassing at $500^\circ C$ followed by cooling to $300^\circ C$ results in traces (13b) and (13c), respectively. An estimate of the half widths of the two higher frequency bands shows a half-width of 70 cm^{-1} and 90 cm^{-1} at $300^\circ C$ versus a value of 75 cm^{-1} and 120 cm^{-1} at $500^\circ C$. The difference in the half-width bands at 3725 cm^{-1} cannot be considered as significant because of the band overlap with the strong absorbance at 3660 cm^{-1} at these elevated temperatures. Exposing the sample to 4.6 torr

Fig. 12. Transmission Spectra, 2400-4000 cm^{-1} Region,
of $\text{ZrO}_2\text{-C}$, as a Function of Temperature.

12w Spectral trace of water adsorbed at 4.6 torr at 100°C, 2400-4000 cm^{-1} region.

12w' Same, on a 4-fold expanded frequency scale, 3600-4000 cm^{-1} region.

12a Outgassed sample at 400°C, 2400-4000 cm^{-1} region.

12b Exposure of sample to 100 torr oxygen at 400°C, 2400-4000 cm^{-1} region.

12b' Same, on a 4-fold expanded frequency scale, 3600-4000 cm^{-1} region.

12c Sample temperature reduced, in vacuum, to 300°C, 2400-4000 cm^{-1} region.

12c' Same, on a 4-fold expanded frequency scale, 3600-4000 cm^{-1} region.

12d Sample outgassed at 500°C, 2400-4000 cm^{-1} region.

12d' Same, on a 4-fold expanded frequency scale, 3600-4000 cm^{-1} region.

Fig. 13. Absorbance Spectra, 3000-4000 cm⁻¹ Region,
of ZrO₂-C at 400, 500 and 300°C (first cycle).

- 13a Absorbance spectra of sample desorbed at 400°C at 6×10^{-6} torr.
- 13b Desorption temperature raised to 500°C at 3×10^{-5} torr.
- 13c Desorption temperature reduced to 300°C at 2.5×10^{-6} torr.

water at 100°C, a second cycle of outgassing at 500°C and cooling stepwise to 300 and 100°C under vacuum gave results in agreement with the absorbance spectra observed in the previous cycle.

Figure 14. Transmission Spectra, 3300-4000 cm^{-1} (temperature cycling)

Figure 14 shows traces as a function of temperature on a fourfold expansion of the frequency scale. The absorption and desorption of small partial pressures of H_2O at temperatures up to 500°C appear to have resolved the high frequency stretch vibration of O-H species and several sub-bands of the stretch frequency of H-bonded water. The very first outgassing of the untreated discs at 100°C indicates that the high frequency band in (14a) occurs at 3760 cm^{-1} with no further resolution of bands at lower frequencies. This band is similar to that observed for the monoclinic sample, $\text{ZrO}_2\text{-G}$. However, after several water adsorption and desorption cycles to 500°C (Figs. 12 and 13) and cooling to 300°C in vacuum, the spectrum of (14b) indicates that the broad high frequency band has taken a marked downward shift from the value in (14a) to an unresolved doublet with a maximum absorbance value at 3725 cm^{-1} . An unresolved doublet likewise appears at 3662 cm^{-1} and 3645 cm^{-1} . The broader sub-bands at 3595 cm^{-1} and 3440 cm^{-1} are also observed here. On further cooling to 100°C the trace (14c) indicates that the high frequency band divides into two partially resolved bands at 3740 and 3720 cm^{-1} and the broadened band at 3660 cm^{-1} is also evident. This trace (14c) has been lowered by 0.03 units in transmittance to allow for spectral comparison viewing. After a second adsorption-desorption cycle up to 500°C, the spectrum of (14d) at 40°C shows a further decrease in absorbance but with a somewhat better resolution of the absorption bands. A splitting of the band at 3662 cm^{-1}

Fig. 14. Transmission Spectra of ZrO₂-C as a Function of Temperature Cycling, 3300-4000 cm⁻¹ Region (4-fold expansion of frequency cycle).

- 14a First outgassing of sample at 100° C
- 14b Desorbed sample at 300° after first desorption cycle of Fig. 13.
- 14c Desorption temperature reduced to 100°C.
- 14d Desorption temperature reduced from 500°C to 40°C after a second adsorption-desorption cycle.

indicates a poorly resolved shoulder at $\sim 3645 \text{ cm}^{-1}$. The broad bands at 3595 cm^{-1} and 3440 cm^{-1} are also resolved to a greater extent as a result of the temperature cycling. The above band assignments are listed in Table 2.

Table 2. Stretch Vibration Frequencies of
Tetragonal $\text{ZrO}_2\text{-C}$

Spectral Species		$\nu(\text{O-H})$	$\nu(\text{O-D})$
Schematic Representation	Band Type	(cm^{-1})	(cm^{-1})
$\text{Zr}-(\text{O}_{1a}\text{-H})^{(a)}$	$\nu(\text{O}_{1a}\text{-H})_T^{(a)}$	3740	2740
$\text{Zr}-(\text{O}_{1b}\text{-H})^{(a)}$	$\nu(\text{O}_{1b}\text{-H})_T^{(a)}$	3720	2740
$\text{Zr}-(\text{O}_2\text{-H})^{(b)}$	$\nu(\text{O}_{2a}\text{-H})_T^{(b)}$	3662	2690
	$\nu(\text{O}_{2b}\text{-H})_T^{(b)}$	3645	2670
C_2	Bound H_2O	3595	2650
C_3	Bound H_2O	3440	2540

(a) Frequency contribution of surface O-H groups bound to single cation at two different spacings ("free" hydroxyl groups) of the tetragonal phase.

(b) Stretch frequency of bound O-H groups each coordinated to more than a single cation, at two alternate spacings.

Figure 15. Transmission Spectra of H_2O - D_2O Species, 2400-4000 cm^{-1} at 160°C

Spectrum (15a) of the outgassed water treated sample shows the resolution of the 3660, 3595 and the broader 3440 cm^{-1} bands. The pattern obtained after 2 hours of exchange at 800 μ D_2O pressure is shown in (15b). The low concentration of D_2O results in a partial resolution of its sub-bands. Further exchange with 4 torr D_2O produces the trace (15c) where broad bands are observed for both the H_2O and D_2O vibration frequencies. Subsequent outgassing leads to a marked resolution of the sub-bands of both species, (15d).

Figure 16. Transmission and Absorbance Spectra of D_2O Exchange at 300°C

An exposure of 800 μ D_2O at 300°C for 18 hours produced the spectral trace of (16a). The continued resolution of both sets of structure bands and also the reduced overlap between the H_2O and D_2O stretch frequencies is observed. On outgassing, the spectrum of the lower frequency is reduced, resulting in a higher resolution of the spectral sub-bands (16b). An absorbance trace at a two-fold reduced scale factor of the outgassed sample is shown in (16c).

Figure 17. Transmission Spectra, 300°C (before and after D_2O Exchange).

A four-fold expanded frequency trace of the outgassed oxide prior to exchange with D_2O is given in (17a). Following the exchange at 800 μ D_2O (16c) and the subsequent outgassing, the spectrum obtained in (17b) showed a great deal of substructure for the O-H stretch frequencies. The corresponding substructure observed in the O-D stretch frequency region is shown in the inset of (17c) on a two-fold reduced intensity scale. The correlation of the corresponding stretch frequencies for the O-H and O-D species is given in Table 2.

Fig. 15. Transmission Spectra of H_2O - D_2O Species on $\text{ZrO}_2\text{-C}$, $2400\text{-}4000\text{ cm}^{-1}$ Region, at 160°C .

- 15a Outgassed sample at 160°C
- 15b Exchange at $800\text{ }\mu\text{ D}_2\text{O}$ pressure
- 15c Further exchange at 4 torr D_2O
- 15d Outgassed sample at 160°C

Fig. 16. Transmission and Absorbance Spectra of

D_2O Exchange on $\text{ZrO}_2\text{-C}$, $2400\text{-}4000\text{ cm}^{-1}$ Region, at 300°C .

16a Transmission spectra of sample exposed to $800\text{ }\mu\text{ D}_2\text{O}$ at 300°C

16b Desorption of above treated sample.

16c Absorbance spectral trace of (16b), using a 2-fold reduced scale factor.

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Fig. 17. Transmission Spectra Before and After

D₂O Exchange on ZrO₂-C, 2400-4000 cm⁻¹ Region, at 300°C.

(4-fold expansion of frequency scale).

17a Outgassed sample before D₂O exchange, 3200-4000 cm⁻¹ region

17b Transmission spectra of water stretch region of the outgassed sample following the D₂O exchange shown in Fig. 16.

17c Transmission spectra of analogous water bands for D₂O, 2400-2800 cm⁻¹ region (2-fold reduced intensity scale).

DISCUSSION

Monoclinic ZrO_2 -G Spectra

The broad unresolved absorption band observed in the 2400 to 3600 cm^{-1} spectral region is generally attributed to the vibrational frequency contributions of hydrogen bonded polynuclear water molecules adsorbed on oxide surfaces.⁽²²⁾ In H_2O desorption studies, relatively narrow bands at high frequencies have been assigned to the stretching frequency vibrations of hydroxyl groups bound to the cation.^(21,22,23) The asymmetric distribution of forces of dehydroxylated surface oxides produce active sites which are capable of dissociating water molecules. The heat of adsorption derived from heats of immersion for these strongly desorbed zirconium oxide surfaces are of the order of 30 kcal/mole H_2O .⁽¹⁾ The chemisorption of each water molecule satisfies the active surface by forming 2(OH) groups on oxygen lattice sites.

The transmittance spectra of the 2400 to 4000 cm^{-1} traces in Figs. 1, 2, and 3 illustrate the effects on the stretching frequency region of successive adsorption and desorption at 4.6 torr of water at increasing temperatures. The 3760 cm^{-1} band appears as a shoulder in the adsorption-desorption cycles at the higher temperatures. In the same series of spectra the desorption at increasing temperatures leads to a successive depopulation of the lower frequency species; thus bringing about the resolution of the band at 3660 cm^{-1} and the much broader band at 3480 cm^{-1} . The resolution of the latter bands suggests that an increasing desorption of the more weakly bound molecular water occurs. The progressive improvement in the resolution of the observed bands is marked on cooling the desorbed sample from 500°C to 100°C in vacuum (Fig. 4). This improvement

is undoubtedly due to a decrease in torsional motion of the bound species and to smaller thermal contributions of the oxide lattice. Reproducible absorbance traces were obtained on a repeated adsorption-desorption cycle through this temperature range. The transmission spectra of Fig. 5 on an expanded frequency scale further delineates the spectral bands on reducing the temperature of the desorbed sample. The peak values are observed at 3760, 3660, 3580 and 3480 cm^{-1} .

Successive exchanges with up to 4 torr D_2O on the outgassed oxide at 40 and 300°C (Figs. 6 and 7) take place rapidly, indicating that the exchange takes place on the surface. The repeated exchange of D_2O at 300°C (Fig. 7), followed by outgassing, adds effectively to a further increase in resolution of the stretching frequency bands at 3660, 3580 and 3480 cm^{-1} . The additional exchange with D_2O dilutes the bound H_2O species and thus leads to the improved uncoupling of the water sub-bands. At low concentrations of D_2O the absorbance bands of the D_2O species likewise show better resolution. A correlation of the corresponding stretch frequencies for the O-H and O-D species is given in Table 1.

The absorption band at 1600 to 1650 cm^{-1} is associated with the bending vibration of the water molecule bound to the oxide surface. The observed spectra in this frequency region (Figs. 8 and 9) indicate that the band observed at 1590 to 1600 cm^{-1} may be attributed to the presence of bound monomeric water in analogy to the assignment given in matrix isolated water studies.⁽¹⁹⁾ The increases in the adsorption of water leads to an increase in the bending frequency and the absorbance of this band.

Adsorption-desorption isotherms⁽²⁾ have indicated that extensive micropores are present in this zirconium oxide sample. The contributions to the bending frequency peak at values greater than 1600 cm^{-1} may be attributed to multimers of H-bonded water molecules^(19,20) retained in these small pores even at elevated temperatures (Fig. 9). The presence of H-bonded multimers of water molecules is also evident by the appearance of the broad absorbance band in the stretch frequency region (Figs. 5 and 14) below 3600 cm^{-1} .

The bending frequency of the hydroxyl group is expected⁽²³⁾ to lie in the 1000 cm^{-1} region. However, strong absorption bands, attributed to the oxide lattice, masked this spectral region.

Tetragonal ZrO_2 -C Spectra

The transmittance spectra of Figs. 10 and 11 show a remarkable similarity to that observed for the monoclinic zirconium oxide sample in these initial adsorption-desorption cycles. Desorption cycling at the temperatures from 300°C to 500°C (Fig. 12) develops high frequency bands that differ somewhat from the values observed for the monoclinic oxide. A noticeable shift and splitting of the two highest frequency peaks develop on repeated adsorption-desorption cycling.

Absorbance spectra on further thermal cycling in vacuo between 500 and 100°C (Fig. 13) show improved resolution on cooling. Here the maximum absorbance of the high frequency band is resolved at 3725 cm^{-1} and differs markedly from the value of 3760 cm^{-1} obtained in the initial treatments of this wafer. The estimated half widths of the observed absorbance bands here also indicate that the thermal motion of the absorbate and absorbent

influences the respective band widths of the two high frequency stretch bands (Fig. 13).

The transmission spectra of Fig. 14 taken on an expanded frequency scale and at a slower scanning rate show improved resolution of several bands as the desorption temperature is lowered from 500 to 40°C in vacuo. Some splitting of the two highest frequency peaks is evident and will be taken up after further discussion of the molecular structure of these oxides.

The exchange with D₂O results in an improved uncoupling of the broad water bands. The exposure of the desorbed disc to varying pressures of D₂O at 160 and 300°C (Figs. 15, 16) resulted in rapid exchange. The corresponding sub-bands of the O-H and O-D species show improved resolution of the expanded frequency scale of Fig. 17. The correlations between the observed O-H and O-D species are listed in Table 2. The ratio of the corresponding frequencies is in good agreement with the expected value.

The additional complexity in the behavior of the ZrO₂-C sample led to an x-ray diffraction investigation⁽²⁵⁾ of both the original oxide and the pressed disc. The original powder gave the diffraction pattern for the tetragonal phase of ZrO₂. On the other hand, x-ray diffraction lines for both the tetragonal and monoclinic phases were indicated on examining the pressed disc. Further study showed that this transformation was also a function of the severity of grinding.⁽²⁵⁾ The diffraction pattern of the original ZrO₂-G powder corresponds to the monoclinic phase along with a trace of the strongest reflection (111) of the tetragonal zirconium oxide structure. The latter reflection was barely detectable for the ZrO₂-G pressed disc.

The initial spectra obtained on outgassing the $\text{ZrO}_2\text{-C}$ sample at 100°C (Fig. 10) showed a resolved high frequency band at 3760 cm^{-1} , similar to the value obtained for the monoclinic $\text{ZrO}_2\text{-C}$ disc. However, on adsorption and thermal desorption cycling with water, this band shifted significantly to a lower range. The explanation advanced is that the pressure-induced strain to the individual particles of the disc is relieved by the cycling treatment only on the oxide surface. The observed spectra would support the proposal that the surface structure of the $\text{ZrO}_2\text{-C}$ disc reverts back to the tetragonal phase in the region of the bound adsorbate molecules on repeated water cycling treatment. The strained monoclinic structure may remain to some extent below the surface of the individual particles; thus accounting for the observation that the x-ray pattern showed the presence of the monoclinic phase even after thermal cycling of water on the $\text{ZrO}_2\text{-C}$ disc.

The reported crystal structure^(7,8) ($P2_1/C$) of the monoclinic oxide indicates that zirconium has a coordination to 7 oxygen atoms in a somewhat distorted, pseudo fluorite type structure. The spacings occur at the average distances of Zr-O_{II} at $2.21\text{ \AA}$, and Zr-O_{I} at $2.09\text{ \AA}$. The packing of the tetragonal form of ZrO_2 can also be represented by a distorted CaF_2 -type arrangement. The zirconium atom is coordinated to 8 oxygen atoms consisting of two interpenetrating tetrahedra, with two different spacings, namely, at the distances of Zr-O_{II} at $2.43\text{ \AA}$ and Zr-O_{I} at $2.04\text{ \AA}$. The spectra observed in the water adsorption studies are undoubtedly influenced by the differences in the zirconium-oxygen coordination and spacings. Proposed models for the interaction of these two phases with water will be discussed in a separate report.

An analysis of the infrared spectra may be made by examining the similarities and differences in the distorted fluorite packing arrangements for the two polymorphs. It is suggested that the stable configuration on the surface of the zirconia polymorphs consists mainly of exposed oxygen and hydroxy anions in the proper ratio to satisfy the cation charge and the more stable coordination of 8 anions to each zirconium atom. The concentration and statistical distributions of hydroxyl anions bound to the surface are governed largely by the environmental and thermal exposure conditions.

The average particle size of the $\text{ZrO}_2\text{-G}$ and $\text{ZrO}_2\text{-C}$ sample is $210 \text{ \AA}^{(2)}$ and $129 \text{ \AA}^{(1)}$ respectively. Thus we may assume that planar surfaces with periodic low index steps are the major contributors to the absorbate interface. In this instance the corners, edges and dislocations are considered to furnish the more active sites but statistically fewer contributors for hydroxyl formation. The highest observed frequency bands are considered to be due to chemisorbed hydroxyl anions and are present at lower concentrations for both of these polymorphs. These bands are assigned as "free" hydroxyls bound to a single zirconium, $[\text{Zr}(\text{O-H})]$, on these more active sites. Furthermore, it is geometrically feasible for water molecules to form H-bonds to the oxygen atom of the "free" hydroxyl. We designate this schematically as $[\text{Zr}-\text{O} \cdots \text{H}_2\text{O}]$. The donor water, H-bonded to the oxygen atom of the "free" hydroxyl, polarizes the hydroxyl group and thus reduces its vibration frequency. This assignment is based on the infrared^(26,27) and structure^(28,29) data for the anhydrous and hydrated compounds, LiOH and $\text{LiOH} \cdot \text{H}_2\text{O}$. A neutron structure determination⁽³⁰⁾ of the monohydrate shows that the hydrogen atoms of two water molecules are

H-bonded to each of the oxygen atoms of the hydroxyl groups without appreciable distortion of the tetrahedral conformation of the water molecule. The infrared data^(26,27) indicate that the monohydrate reduced the hydroxyl stretch frequency by about 100 cm^{-1} .

The sites available for hydroxyl binding on the surfaces of the low index planes are statistically more favorable. The frequency band at 3660 cm^{-1} emerges with the largest total absorbance when the less strongly bound water molecules are desorbed. Water molecules H-bonded to the "free" hydroxyl groups are considered to be responsible for the increased overlap of its stretch frequency with the 3660 cm^{-1} band.

These observations lead us to assign the 3660 cm^{-1} band to surface hydroxyls on planar surfaces. Each of these hydroxyl groups occupy an oxygen site on a low index face and are thus coordinated to two or three zirconium atoms. We represent this schematically as: $\begin{matrix} \text{Zr} \\ \text{Zr} \end{matrix} > (\text{O}_2\text{-H})$. Thus in the (100) plane a hydroxyl group may be formed on the surface coordinated to 2 cations and in the (111) plane to 3 cations. It is assumed that the 3660 cm^{-1} band is broad enough to include the stretch vibration frequency of the hydroxyl group shared by 2 or 3 zirconium atoms. Steric restrictions prevent an analogous hydrogen bonding of the water molecule to the oxygen atom of this hydroxyl group, as appears for the "free" hydroxyl.

The much broader lower frequency bands that emerge in the desorption studies are attributed to strongly bound water species but are more uncertain in assignment as to specific binding types and sites. The frequencies of the broad sub-bands, G_2 and G_3 , are similar to multi-molecular H-bonded water bands derived from infrared⁽¹⁵⁾ and Raman⁽¹⁶⁾ studies of $\text{H}_2\text{O-D}_2\text{O}$

mixtures. Differences in assigned values can be attributed to the influence of the solid surface interaction with the absorbate.

The apparent splitting of the high frequency peaks observed for the $\text{ZrO}_2\text{-C}$ (Figs. 14 and 17) may be attributed to the structure of the tetragonal phase. For this structure, the two interpenetrating tetrahedra of anions about each zirconium at two different spacings offers two alternate sites for the distribution of oxygen and hydroxyl species. Thus, band splitting is observed for these "free" hydroxyls with two different force constants. These are designated in Table 2 and are represented schematically as $\text{Zr}-(\text{O}_{1a}-\text{H})$ and $\text{Zr}-(\text{O}_{1b}-\text{H})$. Surface hydroxyls likewise coordinated at two alternate spacings to more than a single zirconium atom are assumed to produce the observed band splitting at 3660 cm^{-1} . The broad sub-bands, C_2 and C_3 , are assigned to bound water species on the surface but perhaps even more strongly held in the micropores of these oxides.⁽²⁾

The D_2O exchange study of Figs. 16, 17 and 18 demonstrates that a resolution of the sub-bands is enhanced. The observed ratios of $\nu(\text{O-H})/\nu(\text{O-D})$ are likewise in good agreement with theory (Table 2).

The I.R. spectra of pressed discs of the monoclinic and tetragonal zirconium oxides⁽¹⁾ were observed at 120 and 250°C by Erkelens. The monoclinic oxide preheated at 400°C showed the presence of high frequency bands at 3726 cm^{-1} (weak) and 3760 cm^{-1} (strong) and a very broad band below 3500 cm^{-1} . The tetragonal sample preheated at 600°C gave a strong band at 3728 cm^{-1} and a broad band below 3600 cm^{-1} . A reported⁽⁴⁾ weak band at 3815 cm^{-1} appears to be spurious. The powders were stated to have been pressed with 10 tons but no particle sizes were indicated. It is likely

that the latter sample consisted mainly of the tetragonal phase. At any rate it is our experience that the development of details in the sub-band spectra would require thermal cycling with water.

SUMMARY

Thermal desorption spectra of low concentrations of water on large surface area oxides appear to be analogous to matrix freezing studies of adsorbed gases. (19,20) Although low concentrations of species are affected in both instances, the thermal contributions from the absorbate and absorbent in this study result in much broader spectral bands.

The stretch frequency bands resulting from the dissociative adsorption (rehydroxylation) of water molecules on the two polymorphic forms of zirconium oxide indicate that differences exist in the surface forces of the respective oxides. The spectral traces resulting from desorption cycling at temperatures up to 500°C show a large reduction of the broad stretch frequency bands due to molecular water and improved resolution of the spectral bands of chemisorbed species.

The high frequency bands, with relatively narrow half widths, are assigned to the stretch frequency of chemisorbed hydroxyl anions. The highest spectral bands are assigned to the "free" hydroxyls bound directly to a single cation at a lattice site. The band width and intensity due to this species are affected on exposure to relatively low pressures of water vapor. This is attributed to the geometric accommodation of a donor water molecule to H-bond to the available unshared electrons of the "free" hydroxyl anion.

The surface hydroxyl anions coordinated to more than a single cation are positioned at available oxygen lattice sites on a given face and are thus incapable of accepting a proton from a donor water molecule because of steric factors. Apparently the surface hydroxyl anions are present in larger concentrations as noted from their greater spectral absorbance in both of these zirconia preparations.

The resolution of the broader spectra attributed to bound water molecules at the lower frequencies are enhanced by the repeated adsorption and desorption cycling. The partially resolved shoulders at 3580 cm^{-1} and 3595 cm^{-1} for the respective polymorphic oxides may be tentatively assigned to the dipole attraction of the water molecule, to exposed cations, analogous to that observed in hydrate crystal structures.

H-bonded molecular water, with its high extinction coefficient, when adsorbed on these oxide polymorphs results in a broad unresolved frequency band (Fig. 1). Successive desorption cycles at increasing temperatures produce a monotonic decrease in the intensity of the lower frequency region of this band due to lower water concentrations. The decrease in intensity and the lowering of the bending frequency band of water (Fig. 8, 9) is likewise a measure of the desorption of bound molecular water. The partially resolved frequency bands, mentioned above, emerge in the spectrum as a result of the lowered contribution of H-bonded molecular water. In addition to the assignment of these higher frequency bands, a more uncertain assignment is proposed for the very broad sub-bands that are partially resolved at 3480 cm^{-1} and 3440 cm^{-1} (Table 1, 2) on the desorbed monoclinic and tetragonal zirconium oxides, respectively. Molecular water is retained in desorption measurements, as evident by the observed

bending frequency above 1600 cm^{-1} . The stretch frequency of bound water probably contribute to these broad sub-bands. Several types of bound water species may contribute to these broad frequency bands. On extensive desorption, molecular water trapped in micropores of these oxides are likely contributors to these emerging absorbance bands. The dipole interaction of water molecules with donor surface hydroxyl anions is considered to be weak;⁽³¹⁾ and thus, is an unlikely contributor to these bands on the extensively desorbed oxides. However, this weak interaction may be effective in binding water on exposures of the hydroxylated oxide to small partial pressures of water. Further spectroscopic studies of "titrations" of hydroxylated surfaces with other molecular species may shed additional understanding and identification of the various active surface forces on these oxides. The latter knowledge would be useful in evaluating the catalytic capability of these tetravalent high surface area oxides.

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