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SURFACE ANALYSIS BY FOURIER-TRANSFORM INFRARED
(FTIR) SPECTROSCOPY

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August 12, 1981

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Work performed by Union Carbide Corporation, Nuclear Division
for the Department of Energy under Contract W-7405-eng-26

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ABSTRACT

As part of a cooperative study with Group CMB-5, Los Alamos National Laboratory (LANL), a diffuse-reflectance capability for the Fourier transform infrared spectrometer at the Y-12 Plant Laboratory has been implemented. A sample cell with a 25° to 400°C temperature-controlled sample stage and an ultrahigh-vacuum (UHV)-to-atmospheric pressure gas-handling capability has been developed. Absorbance of light from the spectrometer beam, resulting from the beam being scattered from a powder sample, can be measured. This capability of detecting molecular species on and in powders is to be used to study chemisorption on actinide and rare-earth metals, alloys, and compounds. Cell design is described along with experiments demonstrating its performance in detecting moisture absorption on uranium oxide, moisture and carbon dioxide absorption on the lithium hydride/hydroxide system, and carbon dioxide absorption on potassium borohydride.

INTRODUCTION

A cooperative study was initiated with Group CMB-5, LANL, to study the chemisorption of a variety of chemical species on actinide and rare-earth metals, alloys, and compounds. The immediate goal of this study is to devise a method or methods for measuring the infrared absorption or emission spectra of molecular entities chemisorbed on

surfaces or in thin films while these surfaces are exposed to gases at pressures in the range of 1 Pa to 100 kPa. The long-range goal of the study is to integrate these infrared analysis techniques with existing gas volumetric, gravimetric, and spectrometric techniques used at the Oak Ridge Y-12 Plant^(a) to characterize the oxidation and hydriding of uranium.

Fourier transform infrared (FTIR) spectroscopy possesses two primary advantages (the multiplex or Fellgett advantage and the throughput or Jacquinot advantage) over conventional infrared methods.¹⁻² These advantages effectively enhance the sensitivity of the spectrometer to a level where trace analysis is practical. A number of techniques have been considered for these "surface analysis" experiments including attenuated total reflectance (ATR), diffuse reflectance (DR), and emission (E) spectroscopies. Diffuse reflectance was chosen because it was the most passive and, in general, the most applicable to gas-solid reactions. The optical components for DR were commercially available from Harrick Scientific Corporation and an evacuable DR cell was being developed for these optical components. The problem of developing a gas-handling system with infrared windows attached by UHV seals is common to DR, ATR, and E spectroscopies, and the latter two spectroscopies may be implemented later to achieve enhanced sensitivities for specific experiments.

(a) Operated by the Union Carbide Corporation, Nuclear Division, for the Department of Energy.

This report describes the design and testing of the UHV-DR cell and gas-handling system that allows the infrared absorption spectrum of a powder to be maintained at some controlled temperature between 25⁰ and 400⁰C and which permits exposure to various reactive gases at pressures ranging from 1 Pa to 100 kPa. Several experiments are described that demonstrate the use of the cell to monitor gas-solid reactions. These include:

1. The absorption of H₂O on UO₂;
2. The hydrolysis of LiH to LiOH and LiOH·H₂O followed by the reaction of LiOH with CO₂ to form carbonates; and
3. The reaction of KBH₄, a specific reducing agent for carbonyls, with CO₂.

PRESENTATION OF EXPERIMENTAL WORK

The DIGILAB FTIR system used for these experiments consisted of two spectrometers (an FTS-15B and an FTS-15C) operated by a single Data General NOVA-3 computer with two 1.2-million word Diablo 31 disks for data. The normal operating mode and principles of operation have been reported.³ The Model DRA-SID DR accessory designed by Harrick Scientific Corporation for an evacuable cell is shown along with the cell in Figure 1. The normal transmission beam of the FTS-15C spectrometer is intercepted by mirror A and reflected by mirror B to

mirror C, a 6:1 ellipsoidal mirror that focuses the beam onto the sample stage of the DR cell through a ZnSe window (D). Light diffusely reflected from the sample stage exiting the cell through ZnSe window E is collected by ellipsoidal mirror F and reflected into the FTS-15C detector by mirrors G and H. The ZnSe window can be seen reflected in mirror F; and the ZnSe window, the sample stage, and the UO_2 specimen are seen reflected in mirror C.

The evacuable cell is shown schematically in Figure 2. The top cover, consisting of a 2 3/4-inch ConFlat Flange to which is attached the window mounts and ZnSe windows, is the only part of the Harrick-designed evacuable cell that has been retained. The ZnSe windows are sealed to the cell with Torr-Seal epoxy. The base flange has been redesigned so that the sample stage heating and temperature control devices are external to the vacuum system. Attached to the gas inlet and exit ports on the base flange are Nupro SS-4H-SW bellows valves with Cajon VCR4 flanges so that the base flange vacuum wall is entirely of welded stainless steel construction and bakable at 400°C. The valves allow the cell to be removed from the gas-handling system and loaded with sample powder in an inert gas chamber. The completely assembled cell is bakable to 150°C, a limit imposed by the Torr-Seal epoxy window seal. Heat losses from the sample stage are such that the exterior of the cell is $\sim 70^\circ\text{C}$ when the sample stage is at 150°C. The sample stage has been maintained at 350°C for three days in the spectrometer and at 400°C for five hours with no degradation of the

cell's vacuum integrity as determined by helium leak testing with a detection limit of $\sim 1 \times 10^{-8} \text{ cm}^3 \text{ (STP) s}^{-1}$. Preliminary investigation of the temperature at the face of the sample stage relative to the heater and control thermocouples may be low by $5^{\circ} - 10^{\circ}\text{C}$ at 400°C and, within that range, is a function of the atmosphere of the cell. Very small (250 μm diameter) sheathed thermocouples are being obtained to monitor the sample stage temperature.

The gas-handling system is shown in Figure 3. The system attached to the DR cell is designed to be used as an UHV system or as a gas circulative system where mixed gases can be circulated through the cell. This system was constructed from available components. New components have been purchased so that a system containing both an MKS 310 BHS 10 and an MKS 310 BHS 1000 pressure sensor will be attached to extend the measurable pressure range from a lower resolution of 0.1 Pa to 160 kPa. The new system will have permanent gas tie-ins to H_2O , D_2O , Ar, CO_2 , and H_2 . Ports will be available for other gases, the length of the flexible coupling between the cell and the vacuum system will be reduced to $\sim 100 \text{ mm}$, and a means of transferring the cell atmosphere from the cell to a 600-mm gas cell for infrared analysis will be installed.

WATER ABSORPTION ON URANIUM DIOXIDE

During the early stages of the DR gas cell development, before the gas-handling and temperature control systems were installed,

preliminary experiments were carried out to evaluate the DR cell as a method of measuring the interaction of uranium dioxide with room air. The results of these experiments are reported in detail elsewhere⁴ along with a microscopic analysis of the uranium dioxide used. Here the results of that study obtained from diffuse reflectance infrared absorbance measurements are summarized.

The uranium dioxide was formed by water vapor oxidation at 80°C of high purity uranium. The black powder which spalled off of the metal ingot (1 cm x 1 cm x 10 cm) was collected in the Pyrex reaction chamber and transferred under pure argon to the infrared diffuse-reflectance cell. The spectra were transformed as the signal average of 2000 co-added interferograms for each case shown in Figure 4. The spectra are sequentially labeled for incrementally increased exposure to laboratory air (A through E) where E corresponds to full exposure through open valves to the cell. The intensity of the band at 2360 cm^{-1} is a measure of the amount of carbon dioxide gas in the chamber (and in turn a measure of the amount of water introduced from the 60 percent relative humidity of the laboratory). The spectrum labeled E was acquired for the subsequent vacuum state.

Band I is due to a wide range of hydrogen-bonded hydroxyl (O-H) entities where the range of hydrogen bond strength gives rise to the broad band from 2400 to 3700 cm^{-1} . Band II is a measure of the molecular water content as a result of the H-O-H bending mode of vibration which is noted at 1599 cm^{-1} for an isolated water molecule

in the gas phase. This band is comprised of two components (1635 and 1565 cm^{-1}) equally displaced from the reference value of 1599 cm^{-1} . This indicates that the molecular water is involved in two modes of hydrogen bonding: (1) electron donor from the oxygen (1635 cm^{-1}) and (2) proton donor from the hydrogen (1565 cm^{-1}). Band III may be due to a H_2O bending mode or may be indicative of a carbonate structure by analogy to the bands observed for sodium carbonate aqueous solutions. Band IV is possibly due to solid-state vibrations for the UO_2 system (765 cm^{-1} for matrix isolated UO_2) perturbed by the ligand fields of the solid. X-ray diffraction shows only weak broad bands characteristic of UO_2 in finely divided form. No indication of other oxides (i.e., U_3O_8) were detected for either the original material or after exposure to air. Band V ($\sim 625\text{ cm}^{-1}$, not shown in Figure 4) is due to the U-O vibrational modes for bulk UO_2 .

Integrated band intensities were compared as a function of air partial pressure, i.e., the band intensity of the CO_2 peak at $\sim 2360\text{ cm}^{-1}$. The integrated intensity of Band I correlated linearly to the carbon dioxide concentration. The results showed that the sorbed water can be categorized into two types: (a) reversibly sorbed water which can be removed in vacuum at room temperature, and (b) energetically retained water that cannot be removed in vacuum. To a good approximation, the distribution of hydrogen bond types was virtually the same for both the tightly bound water and the loosely bound water. In contrast, Bands II and III were not as systematically variable and/or reversible as

Band I. Increased exposure does indeed lead to an enhanced sorbance indicative of an increase in species with little variation as to type (environment of the sorbed water). However, subsequent evacuation removes only a small portion of this ordered molecular water and this component is that characterized by the vibrational frequency of 1635 cm^{-1} , the higher energy component of Band II. The intensity variations for Band III paralleled those of Band II perhaps indicating that this is a surface mode in a perturbed state (nonvacuum) involving an interaction of sorbed water with a surface oxide (or, more realistically, surface hydroxide) entity. Bands IV and V were independent of the exposure conditions as would be expected for UO_2 lattice vibrations.

LITHIUM HYDRIDE-WATER AND LITHIUM HYDROXIDE-CARBON DIOXIDE REACTIONS

Since diffuse-reflectance infrared (DR-IR) spectroscopy is a relatively recent area of research, little has been published to aid in correlating DR-IR absorption spectra with normal transmission infrared T-IR absorption spectra. In order to establish a relationship between DR-IR and T-IR spectroscopy, to establish sensitivity levels for DR-IR absorbances, and to develop techniques for measuring gas sorption while measuring infrared absorption spectra, the following reactions were carried out on a single powder sample of lithium hydride in the DR cell:

This system of reactions was chosen because the gaseous reactants are common in the environment (air) and because the reactants and products are highly crystalline and their infrared absorption bands are well defined.

The LiH powder used for these experiments was typical of that produced at the Oak Ridge Y-12 Plant. The powder (33.1 mg) was poured onto the sample stage of the DR cell in an argon-filled glove box. Prior to loading the cell, the cell had been baked at 150°C for 60 hours while containing a sacrificial sample of LiH and evacuated by an 8-Ls⁻¹ ion pump. During sample loading, the gas-handling system was continuously purged with argon to prevent air exposure.

Figure 5 shows the O-H stretching frequency of LiOH (3675 cm⁻¹) on the LiH powder as loaded (A), during exposure to 1 atm CO₂ which had little effect on the O-H absorbance (B), five minutes after heating the sample to 200°C which eliminated the O-H absorbance (C), and, upon cooling to room temperature and evacuation of the CO₂, which caused the O-H absorbance to disappear (D). Figure 6, Curve A gives the full spectra of the LiH sample after exposure to CO₂ at 200°C, cooling to 25°C, and evacuation of the CO₂. This spectrum appears to be a typical LiH spectrum characterized by the LiH band at 1280 cm⁻¹. A difference spectrum between this spectrum and that of the original spectrum (Figure 5, Spectrum A) shown in Figure 7 indicates that a carbonate line may exist near 1500 cm⁻¹; but, the noise signal associated with the LiH band maximum, i.e., noise resulting from near

total light absorption, makes identification of the line questionable. Spectra A through E, Figure 6, show the conversion of LiH to LiOH resulting from sequential exposure of the sample to 2.5 kPa H₂O vapor pressure over a 55-hour time interval. Following each exposure, the pressure in the 117-mL chamber rose to approximately 10 kPa resulting from H₂ generation whereupon the cell was evacuated and reexposed to water vapor. During these exposures, the growth of O-H band at 3675 cm⁻¹ and the decrease in the LiH band to reveal a possible carbonate band at 1450 cm⁻¹ is readily apparent. The 2707 cm⁻¹ LiOD band was also observed. The gas-handling system had been exposed to D₂O a week prior to these experiments and the D₂O adsorbed on the steel surfaces exchanged with the H₂O vapor. When exposure to water vapor no longer resulted in a pressure rise, i.e., hydrogen generation had ceased, the sample was left exposed to 2.5 kPa water pressure overnight.

The following day the spectra obtained from the sample were severely degraded and the net light throughput for the system was greatly diminished. Examination of the DR cell indicated that the sample had swollen ~ 2 mm in height and was blocking the light path. A portion of the sample was shaken from the sample stage so that an appropriate volume of sample was distributed on the stage. The spectrum of this sample was similar to Spectrum A, Figure 8, and is that of lithium hydroxide monohydrate (LiH·H₂O). Note the O-H stretch for the hydroxyl (3680 cm⁻¹) and hydrate (3570 cm⁻¹) species as well as a hydrogen-bonded band (3500 to 1500 cm⁻¹) and an H-O-H bending band (1590 cm⁻¹). All but the hydroxyl stretching band (3680 cm⁻¹)

could be removed by reducing the water vapor pressure to below 1.3 kPa and reformed by exposure to 2.5 kPa water vapor for ~ 1 hour. All three monohydrate-related bands formed simultaneously and could be decreased simultaneously by decreasing the water vapor by 0.2 kPa increments. Note that the Li-O bands in Figure 8, Curve C, ($\sim 850\text{ cm}^{-1}$) appear significantly different from the Li-O bands observed prior to sample swelling (Figure 6, Curve E) and monohydrate formation.

Figure 9 shows the conversion of LiOH to Li_2CO_3 by reaction with CO_2 . The first dose of CO_2 (13.7 kPa in 9.4 mL at 24°C ; $41\text{ }\mu\text{mol}$) confirms that the 1450 cm^{-1} line (Figure 6, Spectrum E) is a result of reaction of CO_2 with LiOH on LiH (Figure 5, Spectra B and C). This line is characteristic of a symmetrical carbonate species rather than normal Li_2CO_3 which has a split band at 1500 cm^{-1} and a weak line at 1090 cm^{-1} caused by the carbonate ion's environment having a lower symmetry than D_{3h} . The relative-band intensities of the 1450 cm^{-1} line before reaction with CO_2 , and after addition of one, two, or three $41\text{-}\mu\text{mole}$ doses of CO_2 , was 1:4.5:5.5:6, with the final residual pressures over the sample after each dose being 0.2, 0.6, and 1.2 kPa. Since no increase in the CO_2 gas phase absorbance line at 2360 cm^{-1} was observed after each dose had equilibrated, the residual pressure was assumed to be due to water vapor, a reaction product. The 1450 cm^{-1} absorbance changed in width but not in height after the first dose, thus this band absorbance was probably at a "saturation" value after the first dose, and the 1450 cm^{-1} line prior to CO_2

dosing represents less than the 0.2 mole percent of the sample calculated on the basis of sample size (4.7 mmol LiOH), CO₂ dose, and relative-band intensities (Figure 9, Spectra A and B). The O-H stretch absorbance of the original LiH sample (Figure 5, Curve A) which was reacted with CO₂ to produce the 1450 cm⁻¹ absorbance in Figure 8, Spectrum A, must represent less than 0.4 mole percent of the original LiH sample.

After six CO₂ doses of ~ 40 μmol CO₂ (i.e., ~ 10 percent conversion) of the sample, the residual pressure after dosing exceeded the equilibrium vapor pressure of water. Broad, hydrogen-bonded hydroxyl/water bands centered near 3400 cm⁻¹ appeared, the 1450 cm⁻¹ band broadened to higher energies and became more structured, and normal Li₂CO₃ lines appeared at 1090, 1810, 2500, and 2950 cm⁻¹ (Figure 9, Spectra A-E). The reaction was then driven to near completion by blanketing the sample with 100 kPa CO₂ overnight. This resulted in additional sample swelling, and sample redistribution was again required. Figure 10 shows the resulting DR-IR spectra before and after drying at 400°C in vacuum. In an argon dry box, the as-dried product was removed from the DR cell, blended with KBr, and pressed into a pellet for T-IR absorbance measurement. This spectrum and DR-IR spectra of commercially obtained LiOH containing Li₂CO₃ (possibly as a result of air exposure) and Li₂O (containing Li₂CO₃ as a result of air exposure of LiOH) produced by the thermal decomposition of LiOH at 350°C in vacuum are also displayed in Figure 10. Comparison of these spectra indicate that DR-IR absorbance spectra may

be significantly distorted near strong absorbance lines, probably because of changes in reflectivity (refractive index) in those regions. These distortions may cloud interpretation of spectra. On the other hand, weak lines (1090 cm^{-1}) and overtones or combination bands (1810 , 2500 , and 2950 cm^{-1}) are enhanced in the DR-IR absorption spectra and make more bands available for analysis.

POTASSIUM TETRAHYDROBORATE - CARBON DIOXIDE REACTION

In order to investigate other types of gas-solid reactions and perhaps circumvent the gas absorption measurement difficulties associated with water vapor as a reactant or product, as experienced with the $\text{LiH-H}_2\text{O}$ and LiOH-CO_2 reactions, the reaction of CO_2 with potassium tetrahydroborate, a reducing agent that is specific for hydrogenating carbonyl groups, was investigated. The sample consisted of 1.0 mmol of KBH_4 powder that was exposed to 117 mL of CO_2 at 13.60 kPa and 26°C . No reaction was observed at room temperature by pressure drop measurement or by DR-IR absorption spectroscopy. The specimen was heated in the CO_2 environment to 160°C for four hours at which time new absorption bands at 1595 , 1350 , and 765 cm^{-1} were observed. The DR-IR absorption spectra for this experiment are given in Figure 11. Note that the strong absorption bands for the B-H stretching ($\sim 2400\text{ cm}^{-1}$) and bending modes ($\sim 1120\text{ cm}^{-1}$) appear distorted near their maxima. After allowing the system to reequilibrate with ambient temperature, the CO_2 pressure had experienced a net decrease of $0.18 \pm 0.05\text{ kPa}$. The error limits are estimated on the basis of $\pm 1^\circ\text{C}$

ambient temperature variations in the system over the duration of the experiment. The net pressure drop may represent 0.8 ± 0.3 mole percent CO_2 sorbed by the KBH_4 . Figures 12 and 13 show difference spectra between the starting material and the final product, Spectra A and C, Figure 11. These bands agree with the symmetrical (1350 cm^{-1}) and asymmetrical (1595 cm^{-1}) O-C-O stretching frequency and the O-C-O bending frequency (765 cm^{-1}) of a formate ion, OCHO^- . The CO_2 gas absorption at 668 cm^{-1} and 13.41 kPa pressure in the DR cell ($\sim 20 \text{ mm}$ path length) is shown in Figure 13 along with a broad band at 925 cm^{-1} that may be the result of the formation of a borate.

CONCLUSION

A very versatile tool has been developed for monitoring gas-solid reactions by diffuse-reflectance infrared absorption spectroscopy. The major problem of obtaining a reliable and rugged ultrahigh-vacuum-infrared cell has been overcome. When coupled with ion microprobe analysis,⁵ thermogravimetric,⁶ and gas absorption measurements,⁷ DR-IR absorption should prove to be a powerful tool identifying chemisorbed species, such as H_2O and CO_2 and their environments. Diffuse-reflectance infrared absorption spectroscopy is a new and promising field for research, and great care must be exercised in interpreting spectra, particularly in the vicinity of strongly absorbing bands. The enhancement of minor bands and overtone bands may be a surface effect making the technique more sensitive to near surface phenomena.

FUTURE WORK

In the remainder of this fiscal year, the DR-IR absorption spectroscopy system will be used to survey the chemisorption of water and carbon dioxide on as many of the following powders as possible: U, $\text{UO}_{2.x}$, UH_3 , ThO_2 , Ce, CeO_2 , Ce_2O_3 , $\text{CeH}_{2.x}$, Gd, Gd_2O_3 , and GdH_2 . The purpose of this survey is to select the best system and experimental limitations for future study. The gas-handling system will be rebuilt to incorporate a broader range of pressure measurement, shorter connections between the cell and the ion pump, and permanent gas supplies for H_2O , D_2O , CO_2 , Ar, H_2 , and mixed gases.

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Figure 1. HARRICK MODEL DRA-SID DIFFUSE-REFLECTANCE ACCESSORY AND EVACUABLE CELL.

Figure 2. ULTRAHIGH-VACUUM, DIFFUSE-REFLECTION INFRARED ABSORPTION CELL.

*The heater assembly consisted of a 30-watt, 120 V Hot Watt Heater and two sheathed (1-mm D), grounded Chromel-Alumel thermocouples. The tips of which were silver soldered to the inside of the reentrant sample support within the sample stage. The heater was driven by an RFL 76K-1 proportional temperature controller. Temperature was read using a Newport 267B KCl digital pyrometer. The sample stage was adjustable in height by set screws and electroplated with 75 μm of gold.

Figure 3. ULTRAHIGH-VACUUM GAS-HANDLING SYSTEM.

✂ NUPRO Type SS-4H Metal Bellows Valves

□ CAJON Type 4 VCR Fittings

The volume of the pressure gage region when isolated by closing the five valves was 9.4 mL. Opening the valves to the DR-IR cell increased this volume to 117 mL.

Figure 4. DIFFUSE REFLECTANCE INFRARED ABSORBANCE SPECTRA OF URANIUM DIOXIDE POWDER EXPOSED TO INCREMENTAL PRESSURE INCREASES OF AMBIENT AIR.

Figure 5. DIFFUSE REFLECTANCE INFRARED ABSORPTION SPECTRA OF LITHIUM HYDRIDE SHOWING THE O-H STRETCH OF TRACE AMOUNTS OF LiOH (3675 cm^{-1}) UNDER THE FOLLOWING CONDITIONS:

- A. As loaded
- B. At 27°C in 100 kPa CO_2
- C. At 160°C in 100 kPa CO_2
- D. After Steps A, B, and C at 27°C and $< 1\text{ Pa CO}_2$.

Absorbance bands other than the 3675 cm^{-1} line (B and C) are CO_2 gas absorption in the $\sim 20\text{ mm}$ light path of the DR-IR cell.

Figure 6. DIFFUSE REFLECTANCE INFRARED ABSORPTION SPECTRA OF LITHIUM HYDRIDE AS IT IS BEING CONVERTED (A TO E) TO LiOH BY REACTION WITH WATER VAPOR AT 2.5 kPa. SPECTRUM A IS UNREACTED LiH (SPECTRUM D, FIGURE 5); SPECTRUM E IS > 50 PERCENT LiOH.

Figure 7. THE DIFFERENCE SPECTRUM FOR LITHIUM HYDRIDE BEFORE AND AFTER EXPOSURE TO CO₂. SPECTRUM A, FIGURE 5 WAS SUBTRACTED FROM SPECTRUM D, FIGURE 5 (SPECTRUM A, FIGURE 6).

Figure 8. THE DIFFUSE REFLECTANCE INFRARED ABSORPTION SPECTRA OF $\text{LiOH} \cdot \text{H}_2\text{O}$ (A) AND ITS CONVERSION TO LiOH BY EVACUATION (C). THE SAMPLE WAS EQUILIBRATED AT 26°C WITH H_2O VAPOR AT 2.5 kPa (A) 1.6 kPa (B), < 1 Pa (C).

Figure 9. THE DIFFUSE REFLECTANCE INFRARED ABSORPTION SPECTRA OF LiOH (A) AS IT WAS CONVERTED TO Li_2CO_3 (E) BY SEQUENTIAL EXPOSURE TO CO_2 GAS (A-E) AT 27°C . REACTION EXTENT AS MOLE PERCENT LiOH REACTED: A - 0.2%, B - 2%, C - 9%, D - 16%, E - 20%.

Figure 10. INFRARED ABSORPTION SPECTRA OF Li_2CO_3 IN VARIOUS MEDIA.

- A. DR-IR Spectrum of Wet $\text{LiOH} + \text{CO}_2$ Reaction Product.
- B. After Vacuum Drying at 400°C .
- C. T-IR Spectrum Material from B Pressed in KBr.
- D. DR-IR of Air Exposed LiOH .
- E. DR-IR of Li_2O Produced from LiOH Thermally Decomposed at 350°C .

Figure 11. DIFFUSE REFLECTANCE INFRARED ABSORPTION SPECTRA OF POTASSIUM TETRAHYDROBORATE.

A. As-loaded in the DR-IR Cell and Evacuated at 26°C.

B. At 160°C and 13.7 kPa CO₂ Gas.

C. At 26°C and 13.42 kPa CO₂ Gas after B.

Note CO₂ gas absorption lines at $\sim 3700\text{ cm}^{-1}$ and $\sim 668\text{ cm}^{-1}$.

Figure 12. THE COMPUTED DIFFERENCE BETWEEN SPECTRUM C AND SPECTRUM A FROM FIGURE 11 SHOWING THE O-C-O STRETCHING FREQUENCIES OF THE FORMATE ION.

Figure 13. THE COMPUTED DIFFERENCE BETWEEN SPECTRUM C AND SPECTRUM A, FIGURE 11 SHOWING THE O-C-O BENDING MODE OF THE FORMATE ION (765 cm^{-1}) AND A POSSIBLE BORATE BAND ($\sim 925\text{ cm}^{-1}$). THE BROKEN LINE INDICATES THE RESULTS OF SPECTRAL SUBTRACTION WHEN SPECTRUM A IS REPLACED BY A SPECTRUM TAKEN IMMEDIATELY AFTER CO_2 GAS PRESSURE WAS SET.

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