WATER-DEUTERIUM OXIDE EXCHANGE IN POLYMERS
USED IN SPACECRAFT APPLICATIONS

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ABSTRACT

The replacement of water (H_2O) by deuterium oxide (D_2O) and the exchange between atmospheric water and adsorbed or absorbed D_2O were investigated for the polymeric materials Kapton and Mylar using thermal gravimetric analysis (TGA) and infrared (IR) spectroscopy. Replacement of H_2O by D_2O is easily accomplished. However, exposure of D_2O samples to the ambient atmosphere or gases containing H_2O results in rapid proton and deuteron exchange between H_2O vapor and adsorbed D_2O. Replacement of H_2O by D_2O would not be a practical solution to alleviate spectral interferences that would result from water outgassing in spacecraft orbital environments. Maintaining the materials of interest in a dehydrated state is a more reasonable approach.

INTRODUCTION

Water ice formation on satellite optical surfaces has been suggested as a possible cause of decreased sensitivity of infrared sensing devices. For optimum performance, these devices rely on unattenuated signals in the infrared wavelength region where H_2O ice absorption occurs. It has been hypothe ized that the H_2O collects on the cryocooled optical surfaces after outgassing from materials in close proximity to the surfaces. The most likely sources of H_2O are polymeric insulation, such as Kapton, multilayer insulation (MLI), and aluminized Teflon. The suggestion has been made that replacement of associated H_2O with D_2O in the materials of interest would alleviate the problem by isotopically shifting the infrared ice absorption band out of the wavelength region of interest.

In order for the H_2O replacement to be considered a feasible solution to the problem, the following questions should be answered:

1. Is the H_2O-D_2O replacement accomplished easily, and what are the best methods?
2. Once the replacement is accomplished, how difficult is it to maintain the D_2O level?
3. How important are exchange processes between associated D_2O and ambient atmospheric H_2O?

The last question is the most critical. In the condensed phase, proton exchange between H_2O and D_2O occurs just below the diffusion-controlled limit and is, thus, very rapid (Refs. 1 and 2). In addition, the following rapidly established equilibrium is shifted toward the right at room temperature (K_{eq} = 3.94 at 20°C) (Ref. 3):

$$H_2O + D_2O \rightleftharpoons 2\ HOD$$
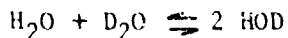
Both H_2O and HOD absorb infrared radiation in the wavelength region of interest. Because of the rapidity of proton exchange, the mixing phenomenon is expected to be limited by surface adsorption and bulk diffusion of water.

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The D_2O-H_2O replacement phenomenon was investigated for Kapton, and to a lesser extent Mylar, by TGA and IR spectroscopy. In addition to atmospheric exposure, N_2 and Ar atmospheres were used to determine if gas adsorption would affect the exchange process significantly.

EXPERIMENTAL

The materials in the investigation were 0.005-in. Kapton and 0.003-in. Mylar sheets examined by means of IR and TGA, and aluminized-Mylar MLI, examined by means of TGA.

The TGAs were performed on a Perkin Elmer TGS-1 thermal balance in both the temperature programmed and isothermal modes of operation. Because of the restricted sample size, it was necessary to cut up the MLI into small pieces, which were then piled in the thermal balance weighing pan. The cutting disturbed the layered nature of the MLI and, as a result, the equilibrium H_2O content might be different from that in the layered configuration. The Kapton and Mylar sheets were simply cut to the appropriate size. The sample weights were generally on the order of 1 mg.

Infrared analyses were performed on a Perkin Elmer Model 467 infrared spectrophotometer. The IR spectra of Mylar and Kapton are shown in Figures 1 and 2. The spectral features in the presence and absence of H_2O and D_2O are included. The Mylar spectrum exhibits a rather small absorption because of the H_2O, and, as a result, only a limited number of experiments were performed. For Kapton, the amount of associated water is larger and, thus, more easily monitored. Despite the larger equilibrium water content, the spectrum of Kapton is complex in the wavelength regions of interest. In order to simplify the spectra, the reference beam of the double-beam spectrophotometer was passed through a sample of "dry" Kapton, which resulted in essentially the spectral features of H_2O and D_2O without interference from the spectral features of Kapton. Two approaches to obtaining these "difference" spectra were employed. In the early stages of the investigation, the "dry" reference sample was stored in an evacuated vacuum dessicator with phosphorous pentoxide as the dessicant. When spectra were obtained, the "dry" sample was placed in the reference beam. In the latter stages of the investigation, a more efficient method was used. A Kapton sample was mounted in a spectrometer gas cell with salt (NaCl) windows. The cell was evacuated to dehydrate the sample and was maintained at low pressure. By means of this approach, the reference sample could be kept in the "dry" state for long periods of time. Both approaches resulted in comparable spectra. Typical spectra obtained by means of the "difference" method are illustrated in Figure 3.

Two approaches were employed in examining the H_2O and D_2O contents of the polymers. In the early experiments in which pre-equilibrium with D_2O was required, the samples were first submerged in D_2O, then mounted in a "film" sample holder and exposed to the ambient atmosphere (relative humidity = 45 to 58%) for specified lengths of time. At the end of the exposure, IR spectra were obtained. It was found that the heating of the samples by the IR beam caused the samples to dehydrate. The rate of dehydration was measured, and the process was determined to have a half-life of approximately 7 min. As a result of this IR stimulated H_2O loss, it was necessary to adjust the experimental procedures to minimize errors. The length of time that the sample was in the IR beam was limited to approximately 2 min, and each data point followed re-equilibration with D_2O and exposure for specified times. By means of this approach, the spectral intensities were accurate to within 15%.

In later experiments in which other than ambient atmospheric exposure was required, the samples were mounted in a spectrometer cell with KRS-5 windows. Appropriate gases were purged through the cell for measured time intervals. The IR spectra were obtained by closing off the cell and placing it in the spectrometer only long enough to obtain the appropriate spectrum, 2 to 4 min. Minimizing IR exposure time and sealing off the cell minimized errors induced by IR stimulated water loss.

The gases used in the investigation were N_2 and Ar. They were both dried by passage through a drying cartridge containing molecular sieves. After drying, the gases were either admitted to the sample cell in the "dry" state or passed over H_2O or D_2O liquid prior to passage through the sample cell. The gas flow rates were approximately 30 ml/min for N_2 and approximately 40 ml/min for Ar. The D_2O was from Merck and Co. and had a deuterium content of 99.7 at% D.

RESULTS

Thermal Gravimetric Analysis

Mylar, MLI, and Kapton were analyzed in both temperature-programmed and isothermal modes of operation. The three materials exhibited two weight-loss processes, the first occurring in the temperature range 300 to 400°K, and the second at approximately 600°K. The first process is attributed to H_2O loss, whereas the second is consistent with sample thermal decomposition. The weight losses resulting from H_2O desorption were determined to be 0.93, 0.37, and 0.24% for Kapton, Mylar, and MLI, respectively.

Isothermal analysis was useful for the Kapton sample but not for Mylar and MLI. For the latter two, instrumental limitations on sample size coupled with low H_2O content resulted in isothermal-weight-loss profiles that did not permit detailed analysis, i.e., the signal-to-noise ratio was very low. For Kapton, isothermal desorption of water at 370°K resulted in a weight versus time profile (Figure 4) that could be analyzed. The curve is exponential with a half-life of 112 sec. The first-order behavior is illustrated in Figure 5. The observation of first-order kinetics is consistent with both bulk diffusion limited and surface desorption limited processes (Ref. 4). In addition, exponential behavior is consistent with just one process; two concurrent processes would give nonexponential results unless the two processes had identical relaxation times.

Infrared Analysis

The IR absorption maxima for H_2O associated with Kapton and Mylar occur at 3550 to 3620 cm^{-1} (2.76 to 2.82 μm) (Ref. 5). The shift to higher energy for the polymer samples implies that the H_2O is absorbed into the polymer matrix rather than being primarily present as physisorbed layers on the surface. Deuterium oxide exhibits a maximum absorption at 2600 to 2700 cm^{-1} (3.70 to 3.85 μm) in Kapton.

The analysis of the H_2O-D_2O exchange for Mylar was limited by the low-equilibrium H_2O content and, thus, small IR signal levels. However, some data were obtained for atmospheric H_2O exchange in a sample that was equilibrated with D_2O. These data are given in Figure 6. The IR absorption that results from the O-H stretching of H_2O and HOD increases with time and reaches approximately 95% of the maximum absorption in 60 min of exposure to the ambient atmosphere.

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For Kapton, the larger equilibrium H_2O content permitted more extensive analysis. The change in the O-H and O-D vibration absorption amplitudes as a function of time for a sample that was equilibrated in D_2O and then exposed to the ambient atmosphere is shown in Figure 7. The shape of the O-H vibration absorption band appears to change with time. In addition, there appears to be a time-dependent shift in the absorption maximum wavelength. These changes can be attributed to differing relative amounts of H_2O and HOD as the D_2O is undergoing exchange. The O-H absorption reaches 75 to 80% of its maximum value in approximately 50 min and 90% of the maximum in approximately 90 min, which is nearly the same as that for Mylar.

The elimination of D_2O from a Kapton sample by "dry" N_2 gas was investigated. The spectral changes are shown in Figure 8. By purging the sample gas cell with N_2 gas, the D_2O is eliminated by means of an exponential process with a half-life of approximately 97 min.

Equilibration of a sample with "dry" gas followed by purging with the same gas passed over D_2O was investigated. The O-D absorption spectral changes are shown in Figures 9 and 10 for N_2 and Ar, respectively. The D_2O band grows in faster in the N_2 case, implying that Ar is more difficult to displace by D_2O than is N_2. The changes in optical density versus time for the data in Figures 8 through 10 are illustrated in Figure 11.

Equilibration of a Kapton sample in air followed by exposure to D_2O in N_2 gas resulted in isotopic exchange that occurred at essentially the same rate as equilibration in D_2O followed by air exposure.

DISCUSSION

The TGA and IR data indicate that H_2O is easily removed from the materials of interest by either heating or exposing to a "dry" atmosphere. In addition, once the material is dehydrated, D_2O can be readily introduced. The major problem that must be overcome is exchange between adsorbed D_2O and H_2O from the ambient atmosphere.

The exchange data indicate that exposure of D_2O equilibrated material to H_2O containing atmospheres must be strictly avoided. The reaction between D_2O and H_2O to yield HOD occurs rapidly and results in a mixture of H_2O, D_2O, and HOD. There should not be a significant isotope effect on diffusion and desorption. As a result, these three species would be expected to outgas with essentially the same rate. Oxygen-hydrogen bonds in both H_2O and HOD contribute to the interferences in the infrared region of interest. Thus, ice formation with significant amounts of HOD would cause IR signal attenuation.

It would be necessary to keep a constant D_2O-saturated atmosphere to maintain the D_2O levels in the materials in the prelaunch environment. A more reasonable approach would be to purge the materials with "dry" air or some inert gas. At the latest possible time, the system could be flushed with D_2O containing gas to equilibrate the materials with D_2O. Maintaining the materials at elevated temperatures, i.e., 50°C, during prelaunch would dehydrate the materials. As in the "dry" air purging, equilibration with D_2O prior to launch would be required.

CONCLUSION

Because of the rapidity of proton exchange reactions between H_2O and D_2O, it would be very difficult to maintain equilibrium D_2O levels in Kapton and

Mylar without employing very stringent controls pertaining to the exclusion of H_2O from the materials. The alternative methods of maintaining the materials in a "dehydrated" state by mild heating or purging the system with "dry" air would appear to be more feasible than maintaining D_2O equilibrium levels. These latter choices require either launching the system in a dehydrated state or equilibrating the material with D_2O prior to launch. Water exclusion measures would also be important for these methods. Although these methods appear to be reasonable a priori, the vigorous exclusion of water from critical spacecraft surfaces would be extremely difficult, if not impossible.

The investigations discussed herein were performed on thin sheet materials so that IR spectral analysis methods could be used.

ACKNOWLEDGMENT

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3. V. Gold and C. Tomlinson, "The Disproportionation of HOD in the Liquid Phase," J. Chem. Soc. D. (1970) 472.
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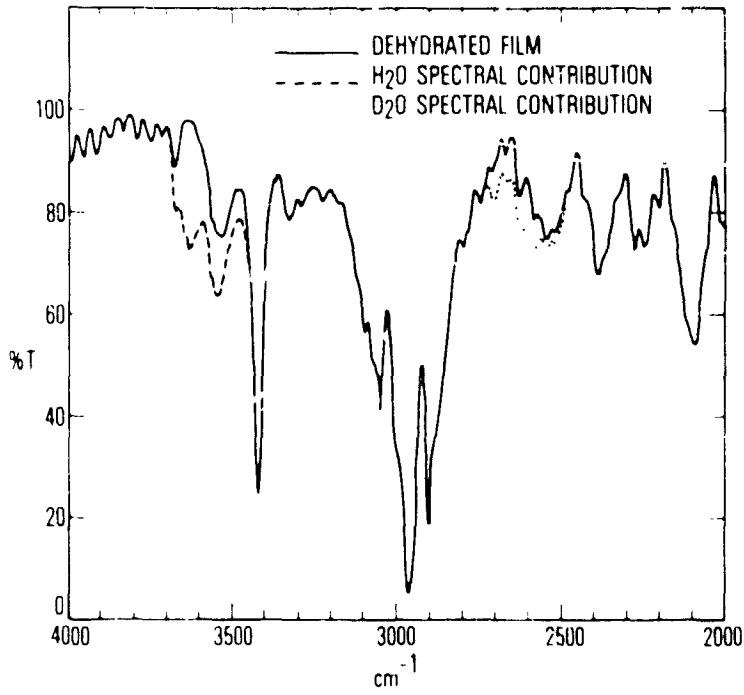
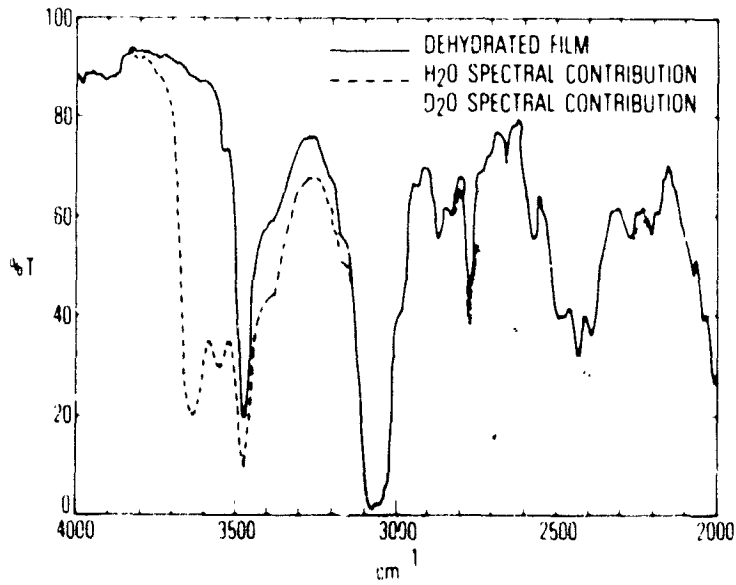Figure 1. IR Spectra of 0.003-in. Mylar Film
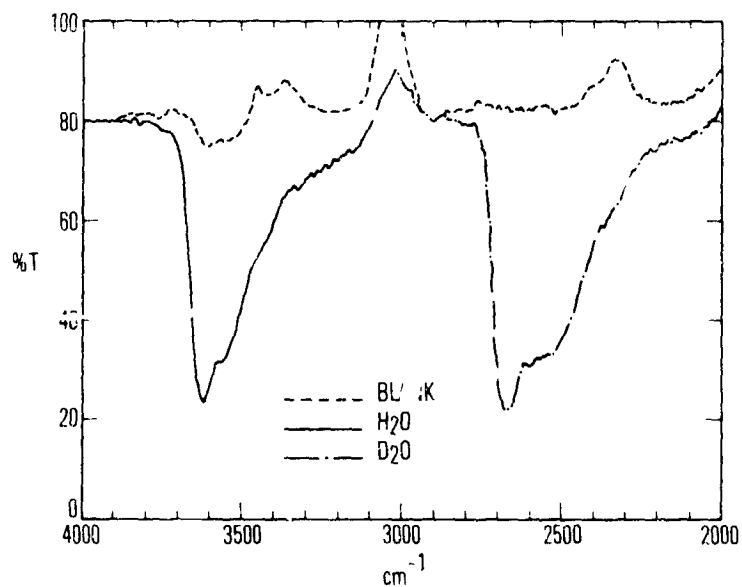

Figure 2. IR Spectra of 0.005-in. Kapton Film

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Figure 3. IR Spectra of 0.005-in. Kapton Film by Difference

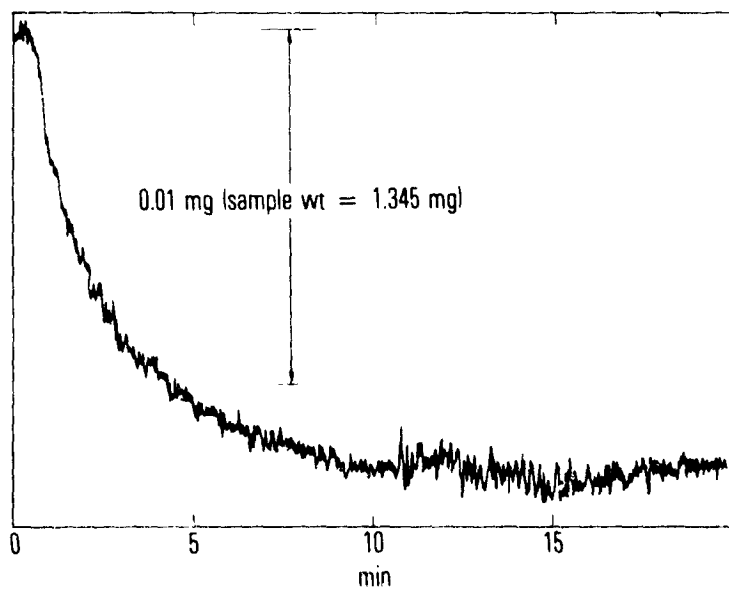0.01 mg (sample wt = 1.345 mg)
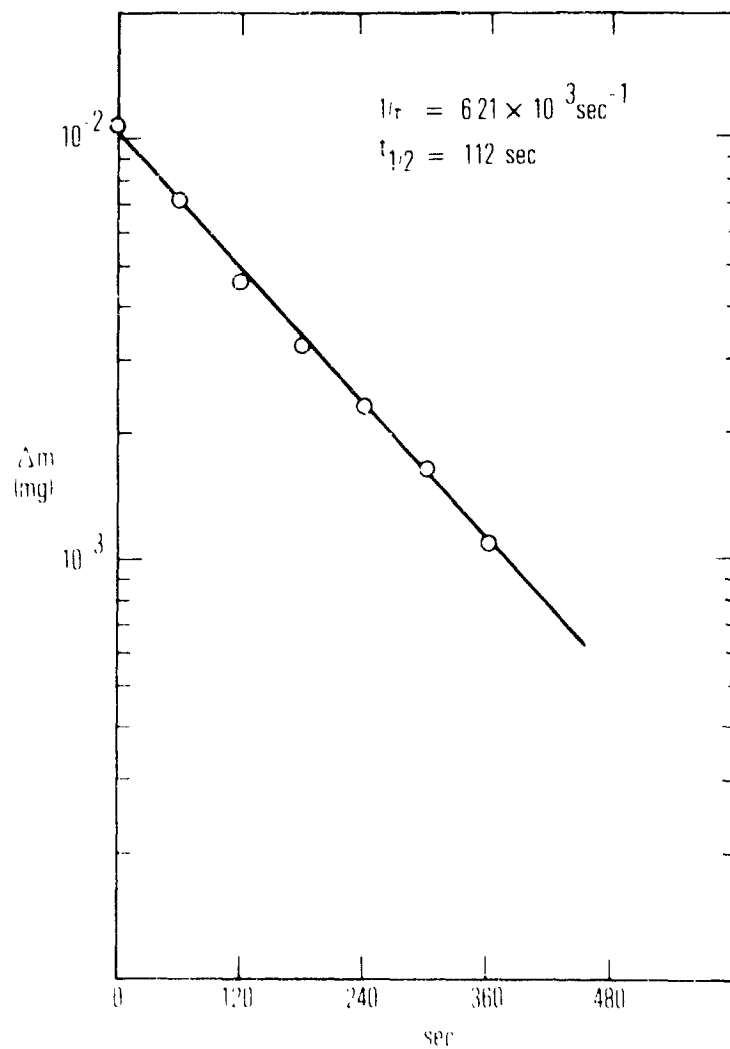
Figure 4. 0.005-in. Kapton Water Desorption at 370°K

Figure 5. 0.005-in. Kapton Water Desorption at
370°K. First order plot with
$1/\tau = 6.21 \times 10^{-3}$ sec^{-1}.

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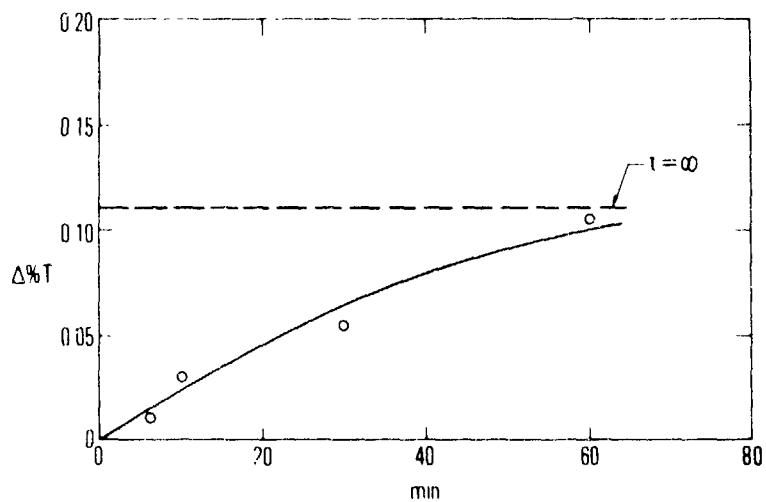
Figure 6. Exchange of Atmospheric H_2O for D_2O in 0.003-in. Mylar Film. $\Delta\%$ transmittance versus time for 3620-cm^{-1} absorption.
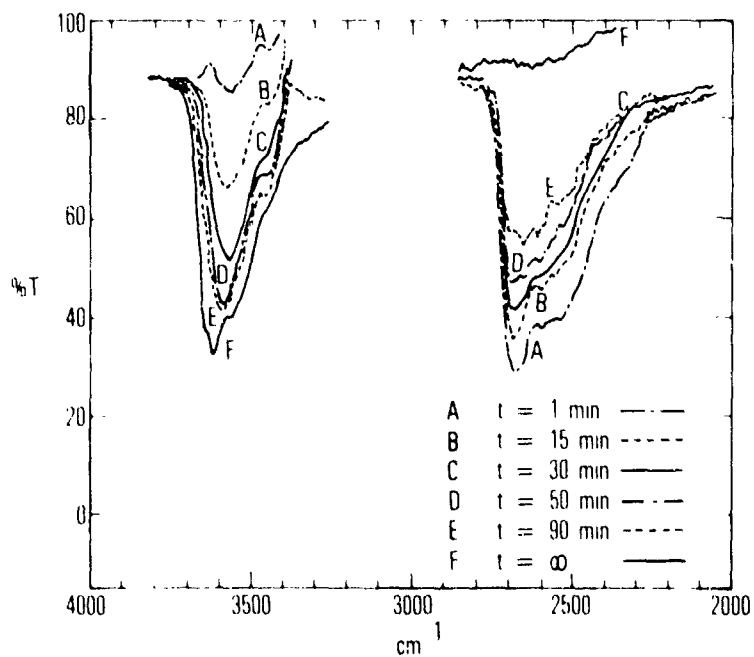

Figure 7. IR Spectra versus Time for Exchange of Atmospheric H_2O for D_2O in 0.005-in. Kapton Film
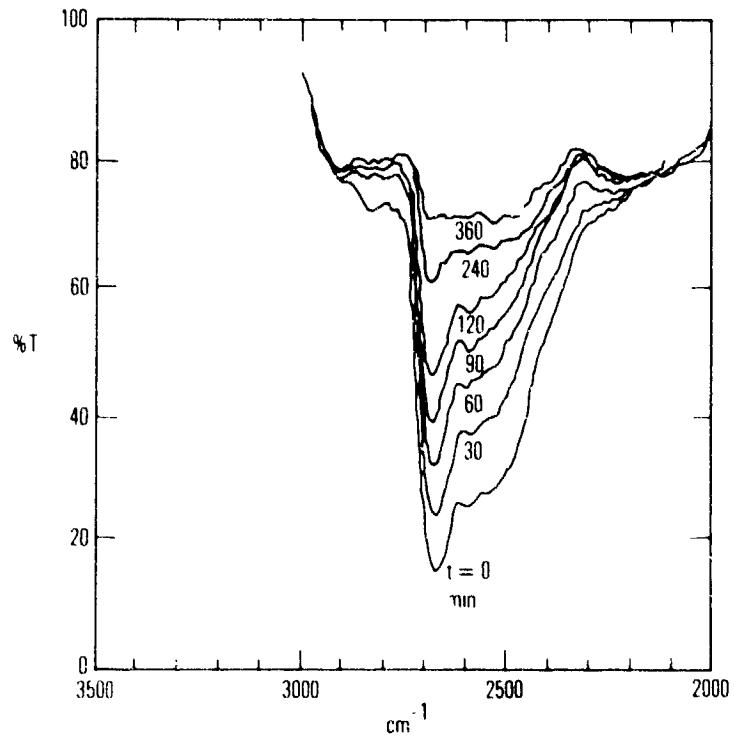
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Figure 8.   IR Spectra versus Time for D_2O Removal from 0.005-in.
Kapton Film with Dry Nitrogen. Nitrogen flow
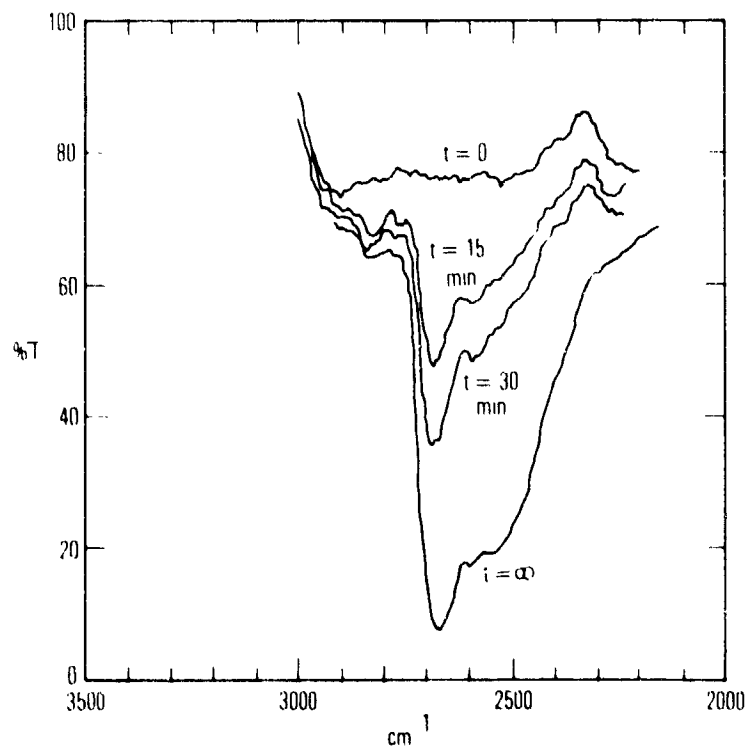Rate = 30 ml/min.

Figure 9.   IR Spectra versus Time for D_2O Uptake by 0.005-in.
Kapton Film. Nitrogen gas passed over D_2O at
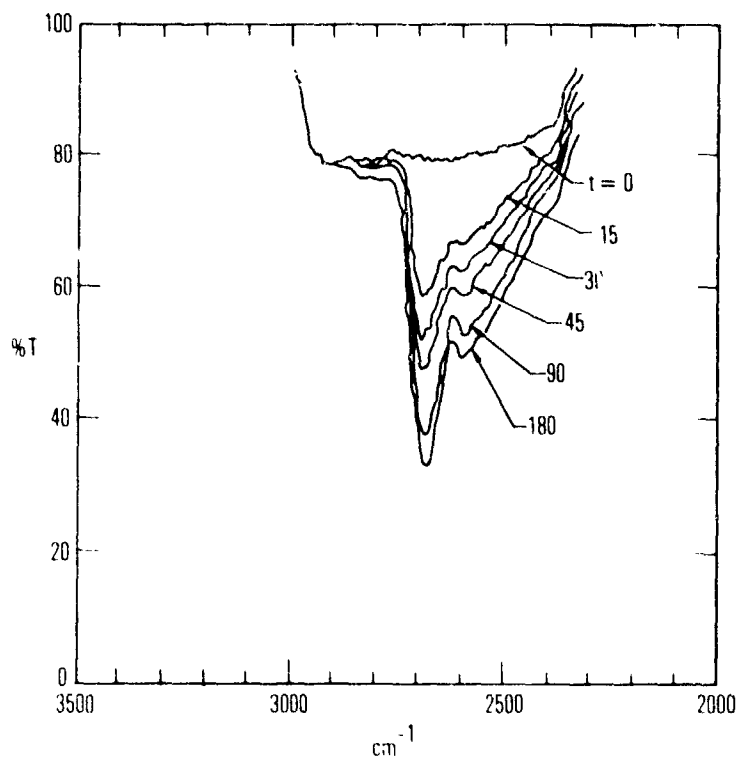30 ml/min flow rate.

100

80

60

%T

40

20

0

3500   3000   2500   2000

cm^{-1}

t = 0
15
3t'
45
90
180

Figure 10.   IR Spectra versus Time for D_2O
Uptake by 0.005-in. Kapton
Film.   Argon gas passed over
D_2O at 40 ml/min flow rate.

D₂O REMOVAL BY "DRY" NITROGEN GAS (30 ml/min)
HYDRATION BY N₂(D₂O) (30 ml/min flow rate)
HYDRATION BY Ar(D₂O) (40 ml/min flow rate)

O D

05

04

03
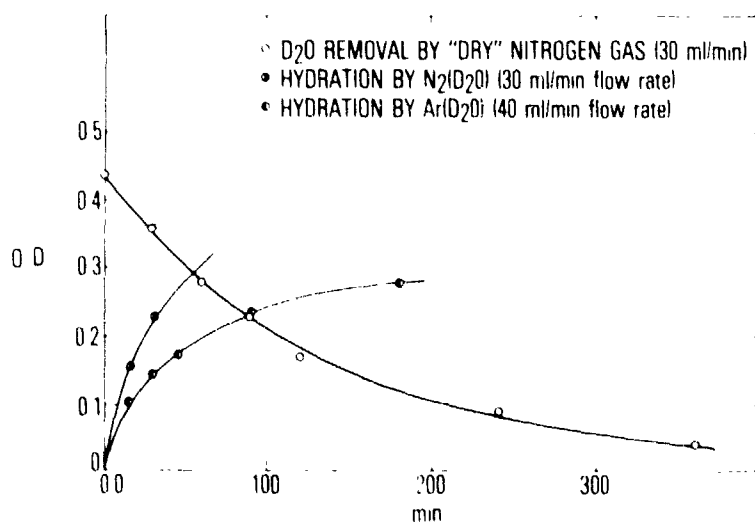
02

01

0

00   100   200   300

min

Figure 11.   Optical Density versus Time for
Dehydration and Hydration of
0.005-in. Kapton Film