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STUDY OF SURFACE FINISHING AND COATING OF DF LASER WINDOWS.(U)
AUG 78 J A HARRINGTON, M BRAUNSTEIN N00014-75-C-0891

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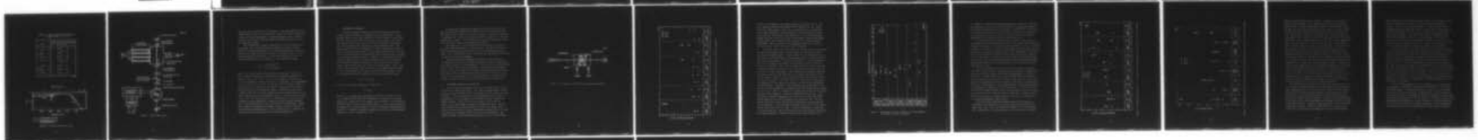

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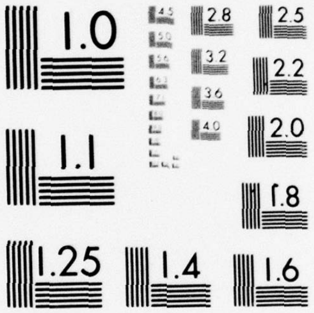

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J.A. Harrington and M. Braunstein

Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, CA 90265

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Final Technical Report
For period 1 June 1977 through 30 June 1978

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This resport summarizes a three-year investigation into the absorption losses in thin film coatings and surfaces of highly transparent materials at 3.8 μm.* The primary emphasis during the first two years was on the minimization of thin film coating losses with the result that it is now possible to achieve film absorptions at DF laser wavelengths of nearly 0.01%/surface. In addition, attenuated total reflection studies performed in cooperation with the Naval Research Laboratory

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yielded information on the nature and cause of surface absorption in highly transparent coatings and bulk materials.

b The majority of this report is devoted to additional studies on surface adsorption and methods that might be used to harden the surfaces of transparent materials. Surface absorption was measured in KCl and CaF_2 that had been selectively contaminated by either H_2O, D_2O, C_2H_5OH, CH_3OH, or NH_4OH. Although increases in surface absorption of as much as 100% resulted for hydrocarbon contamination, a smaller increase than expected resulted for H_2O and D_2O contamination. The surface hardening experiments involved measuring delayed failure in coated (Al_2O_3) and uncoated SrF_2 and CaF_2 substrates. No definitive conclusions could be drawn regarding these results becuase the starting static loads were too high, a~~nd we were not~~ able to complete all the tests.

were not completed.

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SECTION 1

INTRODUCTION AND SUMMARY

This study of surface finishing and coating of DF laser windows began three years ago. It had as its primary goal the minimization of absorption losses in thin film coatings and surfaces of highly transparent materials at 3.8 μm. At the beginning of the program, no studies of coatings at DF laser wavelenghts had yet been made. Today, after numerous measurements of film losses at 3.8 μm on films prepared by our laboratory, coupled with our investigations of surface finishing to reduce surface absorption, *it is possible to achieve film absorptions near* 0.01%/surface. In addition, our fundamental studies on the nature and cause of surface absorption have greatly improved our understanding of the specific impurities that adsorb on the surface of DF window materials. The goals and accomplishments of this three-year research program are summarized below.

A. FIRST YEAR

During the first year, the major emphasis was placed on the study of coating materials that might be suitable for use in the fabrication of low-loss antireflection (AR) and enhanced-reflector coatings at DF chemical laser wavelenghts. To investigate candidate thin-film materials, measurements were made, for the first time, of the absorption in single-layer films deposited on calcium fluoride substrates at 3.8 μm. From this study, we concluded that the lowest absorbing coating materials were ThF_4 and As_2S_3 and that the highest absorbing were oxide materials. In the latter case, low absorption results were precluded by the very large OH^- absorption present in oxide films. At the conclusion of the first year's work, we decided to continue the study of film and surface absorption with particular emphasis on the oxide materials since these materials are especially attractive from the viewpoint of environmental stability.

B. SECOND YEAR

Single-layer, thin-film studies at 3.8 μm continued as the research program moved into the second year. The variety of coating materials increased and lower film absorptions were measured. By the end of this year, it was possible to conclude that several fluoride materials produced the lowest absorbing coatings (e.g., PbF_2, NaF, LiF, YbF_3) and that the oxides still remained too high (approximately 100 times greater absorption than the fluoride films) to be strong contenders, but they remained of interest for their hardness and protective abilities.

Surface absorption of films and substrates was studied using attenuated total reflection spectroscopy (ATR). The films to be studied were evaporated on CaF_2 trapezoids and then sent to the Naval Research Laboratory (NRL) for evaluation. NRL's efforts in measuring and analyzing the film/surface absorption resulted in several important conclusions regarding surface finishing and absorption. One observation was that water and hydrocarbon impurities strongly adsorb on both coated and uncoated CaF_2. Another important result, pertaining to the coated substrates, indicated that certain coating materials, such as ThF_4, adsorb water more readily than do films, such as ZnSe, that seem to passivate the surface against excessive impurity adsorption. This result has particular significance for most applications of DF laser optical components since they see an environment that could ultimately degrade the performance of the surface coating. Knowing that certain materials will reduce environmental degradation will greatly aid future choices of coating materials.

C. THIRD YEAR

During the final year, we decided to continue to pursue hard coating materials and to investigate impurity adsorption further. Selective, low-level impurity adsorption on transparent materials was studied by measuring, calorimetrically, the surface absorption at DF laser wavelenghts. Surface contaminants studied included water and various hydrocarbons adsorbed on KCl and CaF_2. Our results indicate that surface absorption increases substantially when C_2H_5OH or CH_3OH is the impurity environment but that surface absorption is affected much less than expected for H_2O or D_2O contaminants at both 2.8 and 3.8 μm.

The role of thin film coatings in surface hardening was studied by measuring the delayed failure in coated and uncoated CaF_2 and SrF_2. The coating material deemed particularly desirable for these tests was sapphire. A series of small, bar-shaped samples was fabricated and half the samples were coated with Al_2O_3 and half were uncoated. The first tests on polycrystalline SrF_2 were inconclusive because the static load used was too high. Results on single-crystal CaF_2 were also inconclusive.

The results from the first two years of effort are presented in the technical reports and publications listed in the appendix. Section 2 covers the surface absorption studies. Section 3 describes the surface hardening experiments.

SECTION 2

SURFACE ABSORPTION IN KCl AND CaF_2 AT 3.8 AND 2.8 μm*

A. INTRODUCTION

During the past decade, considerable progress has been made in reducing the bulk absorption losses in materials used as DF laser windows. Currently, the lowest loss materials at 3.8 μm are KCl and CaF_2 with bulk absorption coefficients less than 10^{-5} cm^{-1}. However, since surface losses can be much larger than this, surface absorption often remains the dominant contributor to the total absorption.[1] To further determine the nature and source of surface absorption in common low-loss window materials, a systematic study was made of absorption losses produced by the absorption of impurities on KCl and CaF_2. By measuring the small increases in surface absorption at 3.8 and 2.8 μm due to such contaminants as water and hydrocarbons, it is hoped that methods will be suggested to further minimize surface absorption in window materials.

To study the small residual surface absorption in transparent materials, the absorption is calorimetrically measured before and after selectively contaminating the surfaces of KCl or CaF_2. This approach has the advantage of providing the high sensitivity required for measuring small surface absorptions but has the disadvantage of yielding information only at discrete laser wavelengths. Spectral information can be obtained by studying film and surface absorption using internal reflection spectroscopy (IRS).[2,3] This was the method used in the previous study of impurity absorption in films and on the surface of CaF_2 trapezoids.[3] The results of this study clearly defined the water and hydrocarbon bands at 2.8 and 3.5 μm, respectively, on both coated and uncoated substrates, but no further study was made of the particular hydrocarbons involved. This investigation seeks to extend the results of this earlier IRS research to look at specific surface contaminants and the kinetics involved in the

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*The authors wish to acknowledge R. E. Curran for assistance in the calorimetric measurements.

surface adsorption process. Since ATR techniques were not readily available to us, we decided to conduct the selective contamination experiments in our calorimeter chamber and measure the resulting surface absorption using sensitive DF/HF laser calorimetric techniques. The present study supplements the IRS results by providing additional information on specific adsorbates and their effect on KCl and CaF_2.

B. THEORETICAL BACKGROUND

The absorption of infrared radiation by polyatomic molecules is expected to occur at the molecule's vibrational frequencies, which lie closest to the infrared laser frequencies. Since the vibrational energies of common, simple molecules are often quite high, it is not surprising that there are numerous different molecules that can absorb near the DF (3.8 μm) and HF (2.8 μm) chemical laser wavelengths. Several examples of the normal modes of vibration of simple molecules will illustrate this point.[4]

The bent triatomic molecule of the type X_3, XY_2, XYZ, or X_2Y has three vibrational modes. For H_2O, the $\bar{\nu}_1$ and $\bar{\nu}_3$ symmetric and asymmetric stretching frequencies occur at 3651 and 3756 cm^{-1}, respectively, while the $\bar{\nu}_2$ bending mode occurs at 1995 cm^{-1}. It is thus evident that water present on the surface of a material can absorb the HF laser radiation centered at 3570 cm^{-1}. Other molecules in this same classification include O_3, NO_2, SO_2, SCl_2, and Cl_2O although the vibrational frequencies of these triatomic species differ from that of H_2O because the atomic masses differ. Another molecule of particular interest to this study is the XY_4 tetrahedral molecule (methane and NH_4^+ are examples). For this symmetrical configuration, only four modes of vibration are observed. These include, for CH_4, symmetric and asymmetric stretching modes at 2914 and 3020 cm^{-1}, respectively, and two bond bending modes at 1526 and 1306 cm^{-1}. Again, the stretching modes are close to the DF laser frequencies centered at 2630 cm^{-1}. Other examples of molecules and ions that have vibrational modes near 3.8 or 2.8 μm include NH_3, NH_4^+, NO_2^-, and NCO^-.

As the number of atoms in a molecule increases, the number of vibrational modes will increase (the number of vibrational modes will be 3N-6, where N is the number of atoms). In most cases of interest, it is not necessary to identify all the vibrations that can occur in a particular molecule; instead, it suffices to merely identify the group frequencies of common bonds. The group frequencies are those frequencies that are common to many substances which have the same atomic bonds. For example, the C-H stretching vibration occurs near 3020 cm^{-1} in CH_4, C_2H_6, C_2H_2, and C_2H_4. Therefore, this bond can be thought of as being independent of the rest of the molecule. This concept leads to the group or characteristic frequencies of many bonds. These bonds form pieces of the common molecules. Table 1 summarizes the group frequencies of some common bonds as they relate to the problem of surface absorption at DF/HF laser frequencies. For each group frequency, there is associated either the DF or HF laser wavelength. This assignment is based on the multiline spectral output range of these lasers (DF: 3.5 to 4.1 μm and HF: 2.5 to 3.0 μm).

Several features of Table 1 are worth noting. One of these is the isotopic frequency shift that occurs when H_2O is substituted for D_2O. This shift provides a means of studying OH^--type absorption at either HF (OH^- adsorption) or DF (OD^- absorption) frequencies and thus separating out surface absorption from this type of impurity. A second is that most CH absorption occurs near DF laser wavelengths; therefore, hydrocarbon absorption should primarily affect DF absorption.

The spectral features of the two primary surface absorbers, water and hydrocarbons, are shown in Figure 1. This data, taken from the ATR studies of Palik et al.,[33] graphically illustrates the impurity absorption bands and their proximity to the chemical laser frequencies in question. Palik et al.[3] observed these bands on uncoated CaF_2, as shown in Figure 1, as well as on CaF_2 coated with either ZnSe of ThF_4. They also have monitored hydrocarbon adsorption and found that the 3.5-μm CH bands reach saturation on a clean CaF_2 surface after about 200 hr. They discussed this adsorption in terms of chemisorbed and physisorbed layers and concluded that most adsorption was physisorbed after the initial chemisorbed monolayer was formed. For the OH^- band present in Figure 1,

Table 1. Some Vibrational Frequencies of Common Bonds: 2 to 4 μm

Group		Bond Stretching Frequency	
		cm^{-1}	μm
DF	⩾C — H	2960	3.38
	=C — H	3020	3.31
	–S — H	2570	3.89
	–O — D	2759	3.62
HF	≡C — H	3300	3.0
	–O — H	3795	2.64
	≧N — H	3350	2.99

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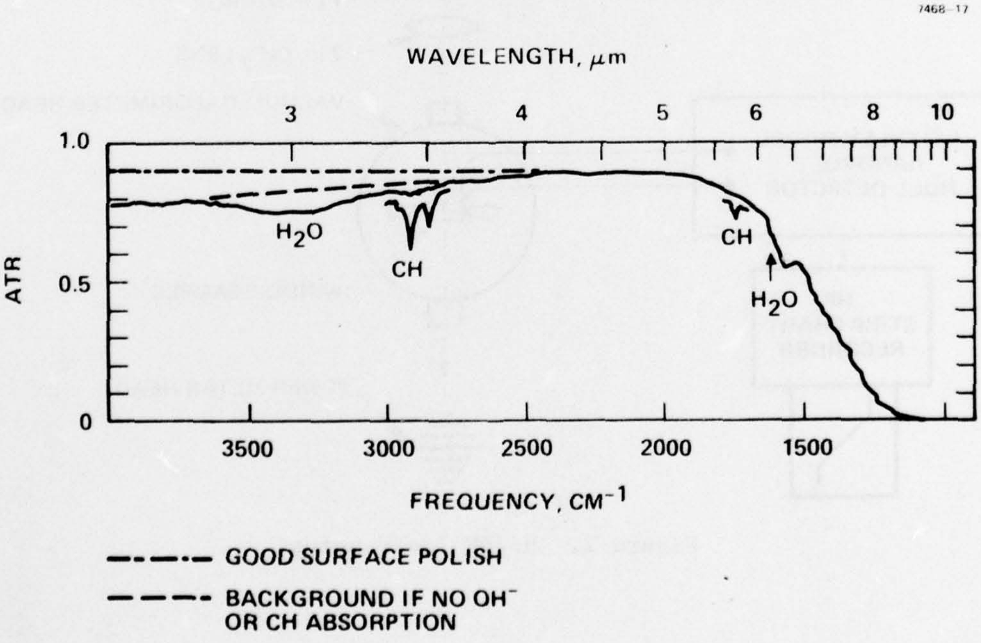

Figure 1. ATR spectroscopy of CaF$_2$.

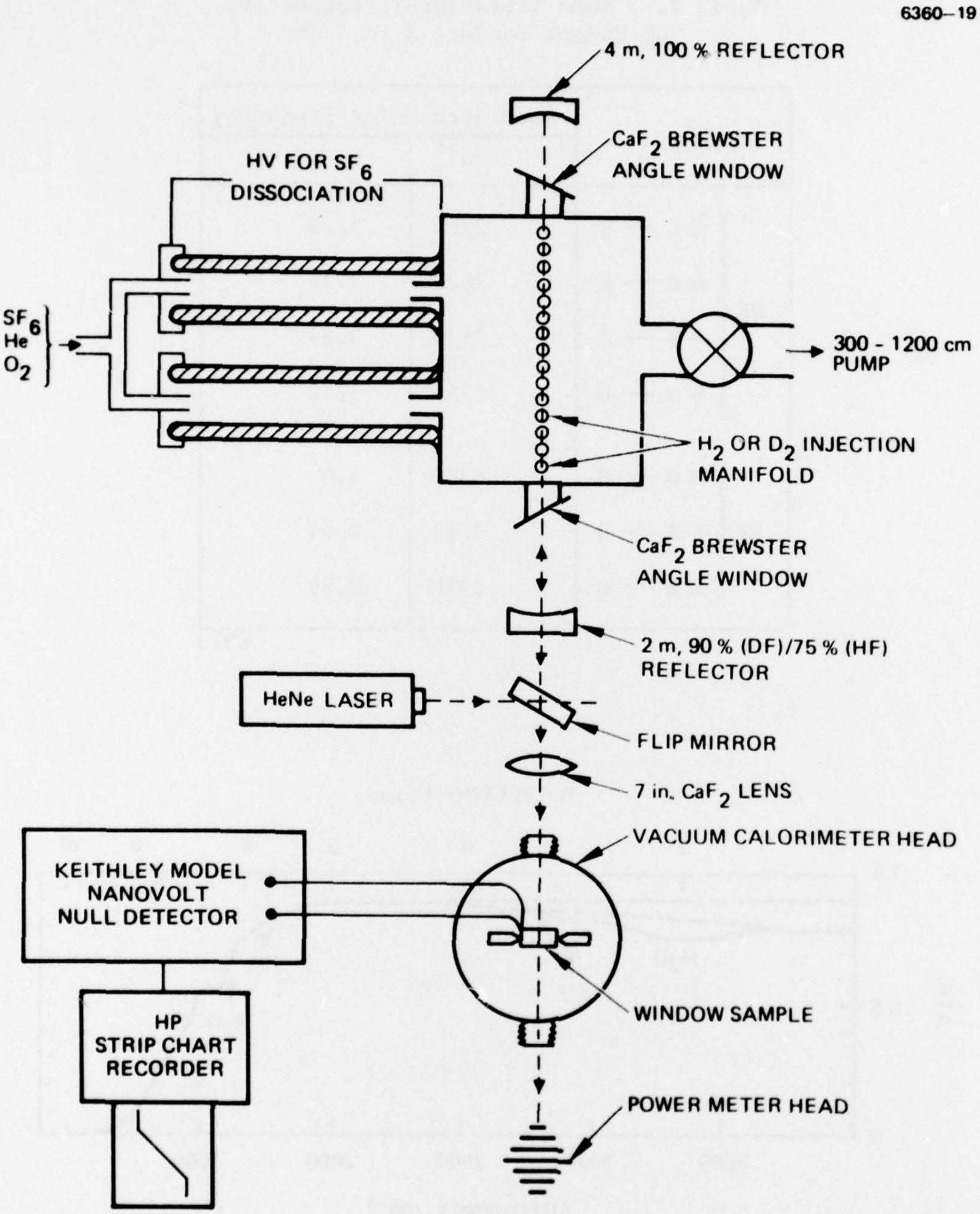

Figure 2. HF/DF laser setup.

they were able to calculate the absorptance at the peak (3600 cm^{-1}) and compare their results to the calorimetric values for typical absorptances in CaF_2 at HF laser wavelengths. Although agreement is only within a factor of two or three, they were able to conclude that water is a surface absorber for CaF_2.

The contribution of impurity absorption to the total absorption at a particular laser frequency has been considered by several authors. Duthler[5] and Flanney and Sparks[6] use a simple phenomenological theory to calculate the absorption due to the wings of an impurity band. To calculate the absorption coefficient β at the laser frequency ω_L due to an absorption band centered at frequency ω_o, a Lorentzian line shape,

$$\beta\ (\omega_L) = \frac{\beta\ (\omega_o)(\Delta\omega/2)^2}{(\omega-\omega_o)^2 + (\Delta\omega/2)^2}\ ,$$

where $\Delta\omega$ is the full width at half maximum, was assumed. Using Eq. 1, Refs. 5 and 6 calculated the concentration of impurities necessary to produce a $\beta(\omega_L) = 10^{-4}\ cm^{-1}$. At 2.7 μm, for example, 0.03 ppm of OH^- or 0.1 ppm of NH_4^+ will produce this level of absorption. At DF wavelengths, $\beta\ (\omega_L) = 10^{-4}\ cm^{-1}$ if as little as 0.01 ppm of SH^-, 0.05 ppm of NH_4^+, or 0.03 ppm of NCO^- is present in the sample. Although their analysis was mainly directed at bulk impurities, similar considerations would apply to surface molecules (the small change in the vibrational frequencies of surface impurities would only slightly affect the concentrations to produce $\beta\ (\omega_L) = 10^{-4}\ cm^{-1}$ as given by Eq. 1). The difficulty in this study of carrying over this formalism to account for observed surface absorption lies in the determination of the concentration of the adsorbate. Therefore, Duthler's and Flannery and Sparks's work will serve to assist in the qualitative interpretation of our data rather than as a means of calculating the surface absorption due to specific impurities.

C. EXPERIMENTAL TECHNIQUES

The small residual absorption in highly transparent solids was measured using the sensitive techniques of laser calorimetry.[7] These methods, which are now quite standard for the determination of IR window material losses, enable absorption coefficients as small as 10^{-6} cm^{-1}. For this particular study, several different calorimetric arrangements were used to study surface absorption at DF and HF wavelengths. One method involved a direct determination of surface absorption through the use of a long, bar-shaped sample.[8] This dynamic method affects the separation of bulk and surface absorption (β_B and S) from the total absorption β_T by noting the different times of arrival at a thermocouple (placed in the center edge of the bar) of surface and bulk heat. A 12.3-cm-long KCl bar provided adequate separation of surface and bulk heat pulse transit times and thus was used in some of the experiments. Most calorimetric studies, however, were carried out on disk-shaped samples (about 2.5 to 4.0 cm diameter x 1 cm thick), and thus β_T was measured. Since the bulk absorption in KCl and CaF_2 is so low at 2.8 and 3.8 μm and

$$\beta_T = \beta_B + S/_{2L} ,$$

where L is the sample thickness, it follows that

$$S \simeq 2L\beta_T .$$

Moreover, the contamination experiments are relative in nature in that β_T is compared before and after contamination. This gives a relative change in β_T that reflects the changes in S, as desired. The calorimeter and DF/HF laser used are illustrated in Figure 2. The vacuum calorimeter was pumped with a sorption pump (10^{-2} Torr) to minimize pumping system contamination. Standard calorimetric analysis for both bar- and disk-shaped samples was used to calculate β_T or S.[7]

In some surface studies, the samples were placed in a heater coil that surrounded the sample when in position in its calorimetric mount. The heater, shown in Figure 3, was used for some of the early vacuum bakeout experiments. The gas inlet shown in Figure 3 allowed the in situ contamination of samples. In all experiments, the impurity gases were evacuated before the absorption measurements were made.

The samples used in this investigation were grown by us (KCl) or purchased from Harshaw Chemical Company (CaF_2). The KCl bar and disk were high-purity materials grown using our reactive atmosphere process (RAP). All of these materials have unusually low bulk absorption and thus are ideal for our surface studies.

The KCl samples were mechanically polished and then etched in concentrated HCl for 30 sec; this was followed by a rinse in isopropanol and a final cleaning in a Freon degreaser. This was the starting condition of the surfaces before any contamination. The CaF_2 disks were lightly rubbed on a lap with Linde B then cleaned by gently rubbing with precipitated $CaCO_3$ slurry, followed by distilled water, and ethanol soak, and finally a Freon degreaser to dry. These polishing an cleaning methods seemed to produce the surfaces that had reproducibly low absorption.

D. EXPERIMENTAL RESULTS AND DISCUSSION

The first material studied was KCl since it would seem to be most susceptible to surface adsorption. The long, bar-shaped sample was measured for several different surface adsorbates, and the results are given in Figure 4. For this sample, the total absorptance ($\beta_T L$), which is proportional to S, is plotted at both 3.8 and 2.8 μm as a function of sample treatment. Since the first run, shown on the far left in Figure 4, was rather high, the sample was cleaned and rerun. The CO_2 gas increased both DF and HF absorption slightly even though little effect was expected since CO_2 has vibrational wavelengths (4.3, 7.2, and 15.0 μm) that are somewhat distant from DF and HF wavelengths. The greater increase in DF absorption may possibly be due to the proximity

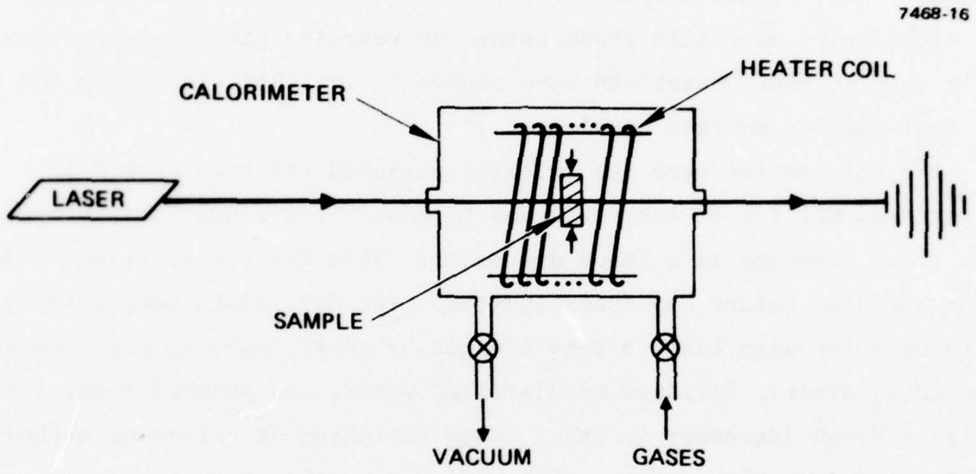

Figure 3. Calorimeter used for surface absorption studies.

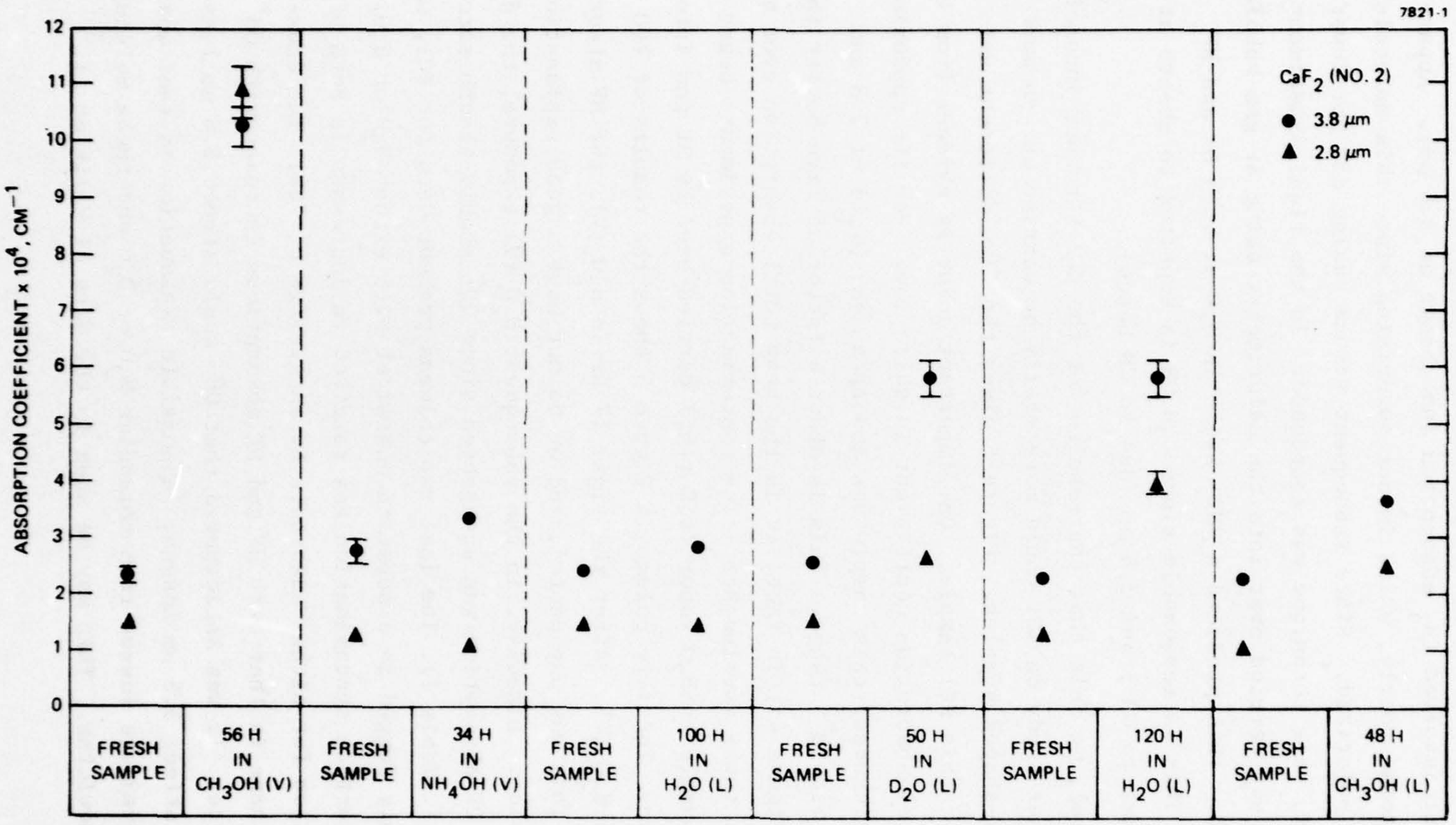

Figure 4. Surface absorption in KCl as a function of surface treatment.

of the 4.3 μm asymmetric stretching frequency of CO_2 near 3.8 μm. The next experiment involved CH_4 adsorption (no change at 3.8 μm). Apparently, CH_4 adsorbs poorly, which is not surprising since this molecule is not highly polarized. Since subsequent vacuum baking did not lower the absorption, this technique was abandoned. In the final experiment, ethanol vapor was carried over into the calorimeter using Ar gas bubbled through C_2H_5OH. This produced a 28% change in $\beta_T L$ at both DF and HF wavelengths. This is reasonable since C_2H_5OH is expected to absorb at both 2.8 μm (due to OH^-) and 3.8 μm (due to CH bonds).

In general, we felt that the results for the KCl bar were inconclusive and that further study on KCl could more easily be carried out on more tractable disk-shaped samples. Figure 5 gives the five different sets of experiments for this KCl sample. One important point is evident from this data. The total absorption coefficient is quite low. For the approximately 0.8 cm thickness, this sample has absorptances ($\beta_T L$) at 2.8 and 3.8 μm in the mid-10^{-5} range. This is about a factor of five better than the KCl bar (Figure 4); in fact, it is the best total absorption ever measured by us at these wavelenghts. The contamination experiments began by exposing the sample to H_2O vapor (65% r.h.) carried over by Ar gas into the calorimeter. The left column in Figure 5 shows the results of 100 hr of exposure to H_2O (V). After the final 17 hr in H_2O (V), the HF absorption dropped. This was unexpected, and we do not have a good explanation for this behavior. Likewise, in the subsequent D_2O (V) exposure, the decrease in the DF absorption was unexpected since OD^- should absorb strongly near 3.8 μm (cf. Table 1). The last two columns present data for KCl, which has been visibly fogged in a separate container with either D_2O or H_2O. This drastic surface contamination has resulted in increases in both DF and HF absorption for either adsorbate by an average of 76%. The unexpected result here is that both HF and DF absorptions increase with OH^- or OD^- adsorbate. It was anticipated that OH^- would affect 2.8 μm losses and OD^- would affect 3.8 μm losses. A possible explanation is that what is being observed are losses from molecular H_2O or D_2O and these molecules have large bandwidths. This may be seen in the data of Palik et al.[3]

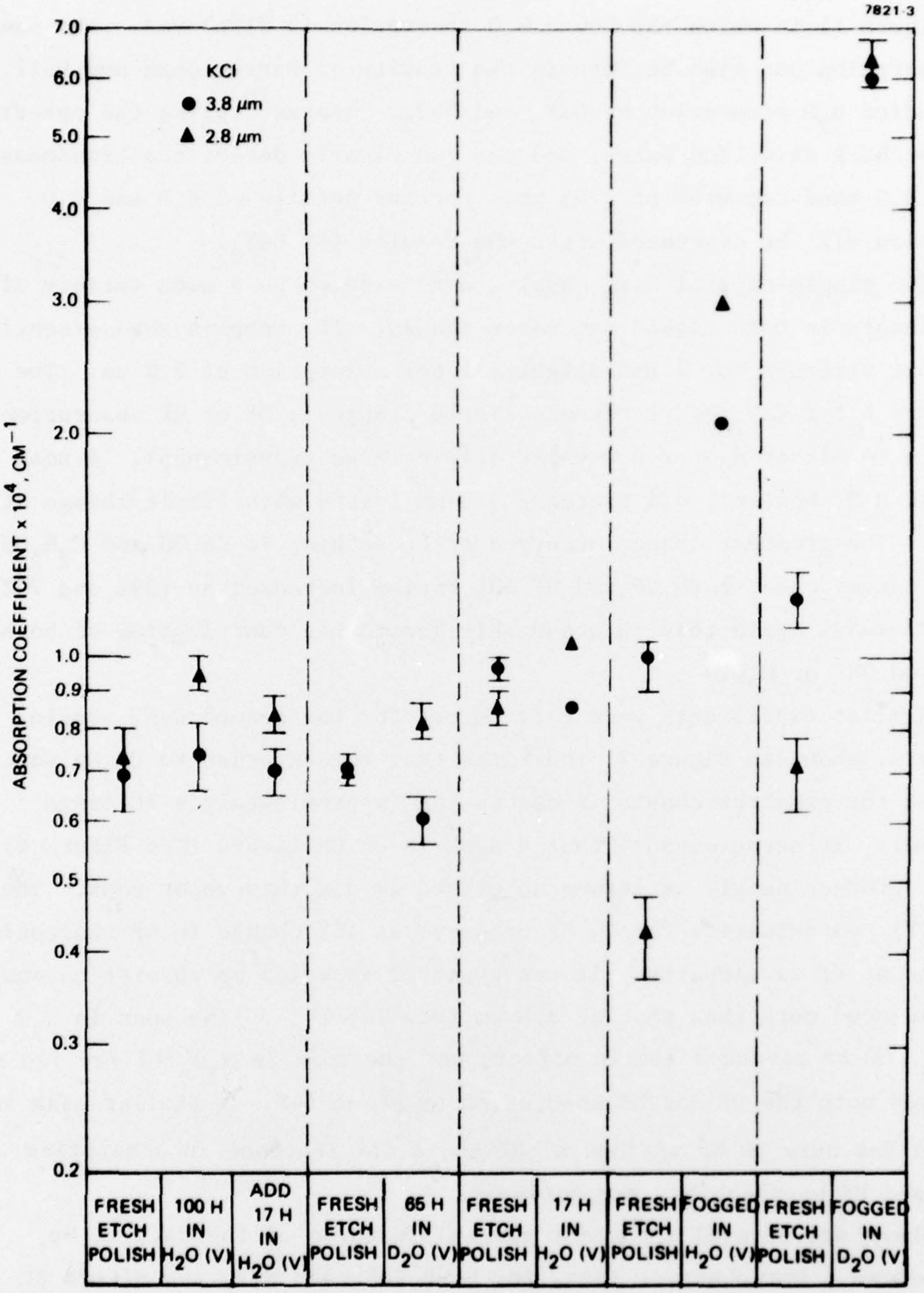

Figure 5. Absorption in KCl at chemical laser wavelengths as a function of surface treatment.

(cf. Figure 1) in which the broad H_2O absorption is displayed. The same H_2O absorption can also be seen in the results of Barraclough and Hall,[9] who studied H_2O adsorption by CaF_2 and BaF_2. Sparks[10] gives the spectrum of 5-μm-thick distilled water, and one can clearly detect the broadness of the H_2O band centered at 2.95 μm. Further details of H_2O and D_2O absorption will be discussed after the results for CaF_2.

Two single-crystal CaF_2 samples were exposed to a wide variety of contaminants in both liquid and vapor phases. The samples were essentially identical although No. 2 had slightly lower absorption at 2.8 μm. The data in Figure 6 for CaF_2 No. 1 reveals little change in DF or HF absorption on exposure to either H_2O or D_2O vapor (first three experiments). A soak for 65 hr in H_2O, however, did increase 3.8-μm losses with little change at 2.8 μm. The greatest change occurred after soaking in CH_3OH and C_2H_5OH. In the latter case, both DF and HF absorption increased by (29% and 70%, respectively). Again this is presumably due to the contribution of both bonds and OH^- or H_2O.

Similar experiments were carried out for the second CaF_2 sample. This data, shown in Figure 7, indicates that the exposure to CH_3OH vapor produced the greatest change in absorption (approximately a 10 times increase). It seems unusual that a soak in CH_3OH liquid (see Figure 6) did not produce nearly as strong an effect as did this vapor soak. The NH_4OH (V) contamination for 34 hr produced an 18% change in DF absorption but none at HF wavelengths. It was expected that 2.8 μm absorption would be influenced more than that at 3.8 μm (see Table 1). The soak in H_2O (L) for 100 hr produced little effect, but the soak in H_2O (L) for 120 hr increased both the DF and HF absorption by about 64%. A similar soak in D_2O (L) for only 50 hr yielded a 56% and a 41% increase in absorption at DF and HF wavelengths, respectively.

There are several important general features of the data to be interpreted. One observes that, for both CaF_2 and KCl, the effect of either D_2O or H_2O is not as pronounced as might at first be expected. This is believed to be at least partly due to the presence of a small

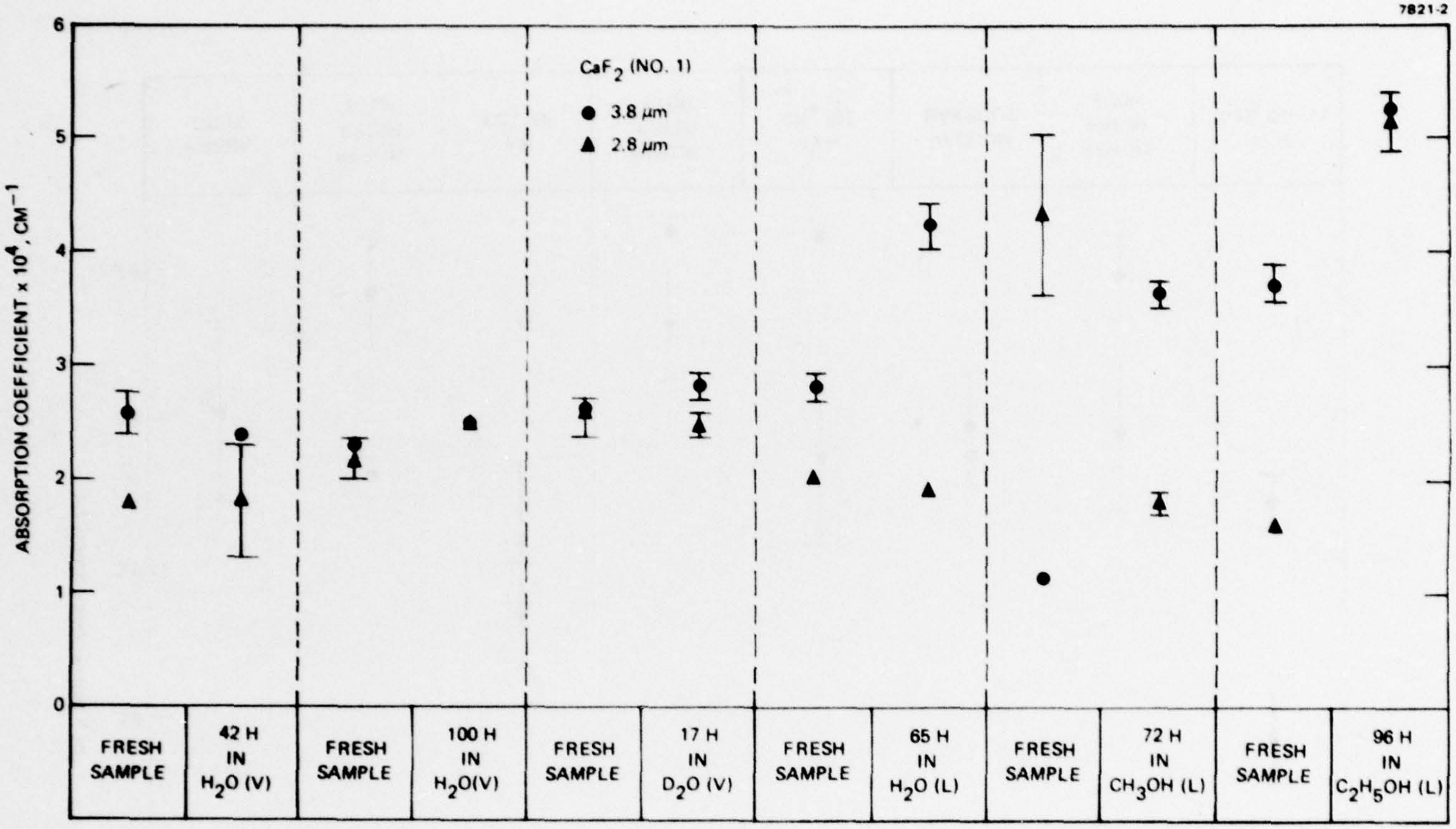

Figure 6. Absorption in CaF_2 (No. 1) at chemical laser wavelengths as a function of surface treatment.

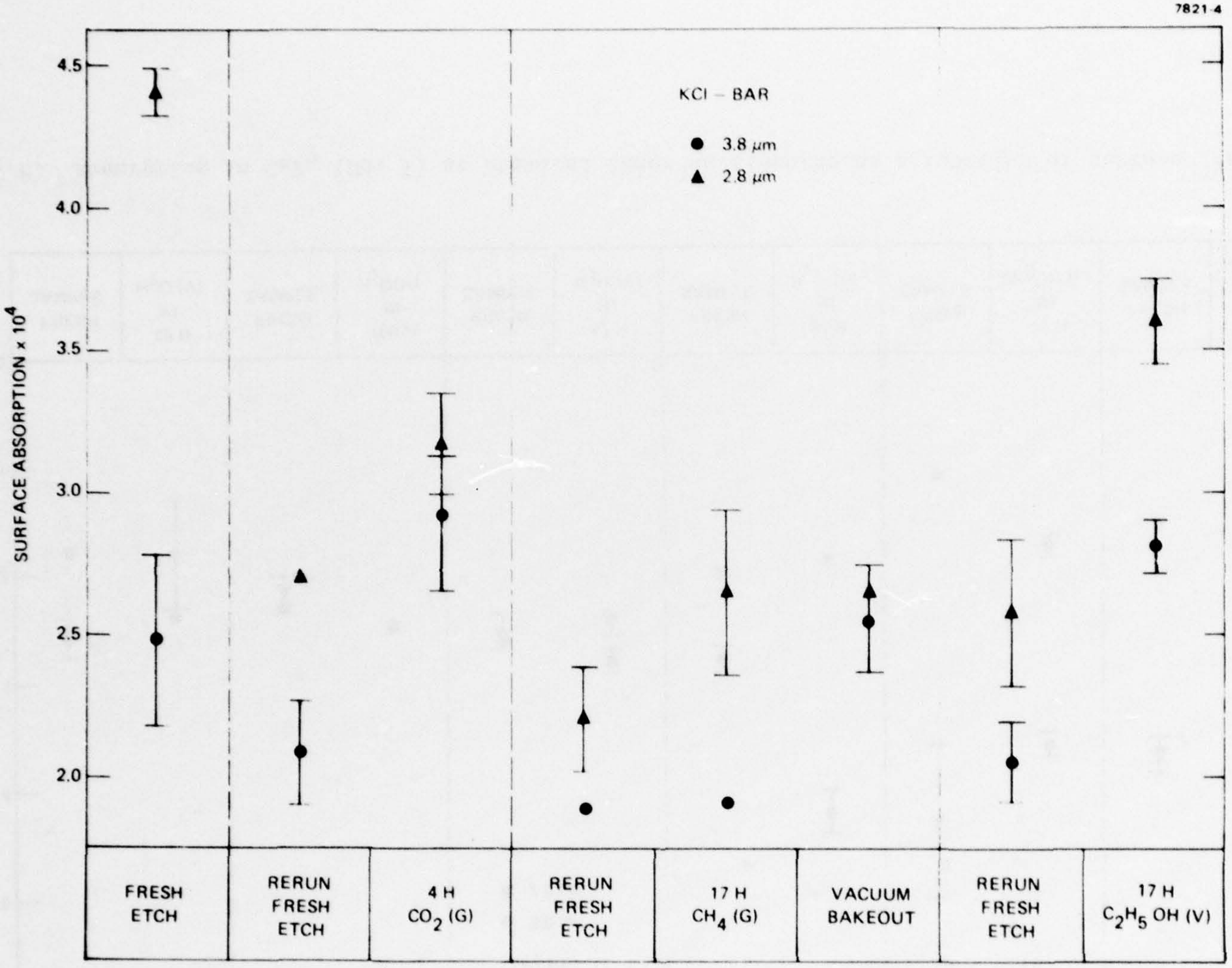

Figure 7. Absorption in CaF_2 (No. 2) at chemical laser wavelengths as a function of surface treatment.

amount of adsorbed water on the surface. Although the exact amount of surface water is unknown, it is estimated to be only a few monolayers thick ($\approx$4 nm) for CaF_2. Barraclough and Hall[9] observed H_2O absorption for CaF_2 and certain alkali halides, but their studies involved pressed powders, which have much greater surface areas than the crystals used here. Nevertheless, Palik et al.[3] estimate that, after admitting distilled H_2O to their chamber containing the CaF_2 trapezoid, a water film comprised of a thin chemisorbed layer ($\approx$0.3 nm) and a thicker physisorbed layer ($\approx$1.0 nm) was formed. They further noted that the physisorbed layer could be removed by pumping at room temperature. Barraclough and Hall, however, indicate that water molecules are bound relatively strongly to CaF_2 and that they cannot be removed by pumping at 300°K. Instead they note that water is desorbed on CaF_2 at 673°K under vacuum. In any case, Palik et al. measured a water absorption of 0.015% per surface in CaF_2 at 2.78 μm. Our value for CaF_2 varies depending on surface treatment (i.e., exposure to either H_2O vapor or liquid). Considering the data from Figures 6 and 7, the HF absorption (assumed all due to H_2O) ranges between 0.004% and 0.01% per surface for samples 0.55 cm thick. This is less than that reported by others but is at least near the estimate of Palik et al. The problem in these comparisons is that, since quantitative data is lacking, only order of magnitude estimates are possible. It seems reasonable to conclude, as did Palik et al., that the absorption at 2.8 μm is related to water absorption.

The observation from Figures 6 and 7 that the absorption at 2.8 or 3.8 μm does not change consistently for either D_2O or H_2O contamination may be explained by the fact that the "fresh" surfaces already contain a thin water film and no further significant water adsorption occurs. Both Palik et al. and Barraclough and Hall observed strong H_2O bonds prior to any vacuum cleaning or baking. Therefore, our CaF_2 already has a thin water layer, and our experiments are designed to detect only additional adsorbed water. Presumably, additional water in the vapor phase is difficult to adsorb. This is verified by Ref. 9 in which it was found that the starting pressed powder disk of CaF_2 has the maximum water absorption and that vacuum heating decreases this absorption. Subsequent re-exposure of the disk to water vapor caused this band to return to the same level as before bakeout. The more extreme surface treatments involving long soaks in D_2O or H_2O yielded, in some cases, an increased absorption. For these cases, it would seem that additional H_2O or D_2O is adsorbed. To confirm these results, the samples should initially be desorbed of water by a vacuum bakeout. The one experiment with KCL involving a vacuum bakeout at $200^{o}C$ for 4 hr was insufficient to remove any water (see Figure 4). Higher temperatures and a cleaner vacuum would be necessary for CaF_2 to produce a clean surface.

The data in Figures 5 thorugh 7 shows that water increases both DF and HF absorption if the samples are exposed for long periods. What seems unusual is the observation that both DF absorption and HF absorption increase by about the same amount, independent of D_2O or H_2O adsorbate. This is contrary to expectations if it is assumed that the absorption is due to OD^- or OH^-. Flannery and Sparks[6] have studied the absorption of OH^- in KCl and, using the simple theory embodied in Eq. 1, have predicted the OH^- concentration necessary to produce $\beta = 10^{-4}$ cm^{-1} at 2.8 and 3.8 μm. They find that 0.03 ppm of OH^- at 2.8 μm and ≈5 ppm of OH^- at 3.8 μm will produce this absorption. This is a difference of more than a factor of 100. Since our results do not indicate a difference even approaching this magnitude, we are forced to conclude that the observed absorption is not due solely to OH^- or OD^-.

The most likely explanation for the observed effect is absorption by H_2O and D_2O. Sparks[10] has considered the absorption by a thin layer of distilled water. The H_2O band, centered at 2.95 μm, is much broader than OH^- and, according to Sparks, is approximately 10 times stronger at 2.8 μm than at 3.8 μm. Sparks has calculated the thickness of water needed to produce an absorptance of 10^{-4} per surface. He finds that only 0.34 nm (approximately one monolayer) of H_2O is required at HF laser wavelengths, but that 4.0 nm is required at DF laser wavelengths. These thicknesses, which reflect the factor of 10 differences just mentioned, are based on a broad multiline laser output, which would more accurately represent our results since our laser operates multiline. Again, however, we do not observe a factor of 10 difference in DF and HF absorption after H_2O exposure for either KCl or CaF_2.

The other contaminants studied include CH_3OH, C_2H_5OH, and NH_4OH. As indicated in Table 1, these impurities were selected because of hydrocarbon or NH_4^+ absorption in the 2.5 to 4.0 μm region. The CaF_2 data in Figures 6 and 7 shows an increase in both DF and HF absorption after soaks in $CH_3OH(L)$ or $C_2H_5OH(L)$ but only a slight increase in DF and no increase in HF absorption after exposure to $NH_4OH(V)$. The increase in both 3.8 and 2.8 μm absorption for the alcohols is reasonable since both CH bonds and H_2O are present.

One reaseon that the contaminated samples may not show absorptions as large as first expected is that the surfaces may be cleaned by the laser beam. It would seem, however, that if this were the case the data taken during the first run would be higher than that taken in subsequent runs. Since this is not observed, it seems reasonable to eliminate laser beam cleaning as a possible explanation.

The multiline output of the laser clearly can affect the absorption depending on the overlap between the laser output and the impurity band. In general, the multiline output will overlap a large portion of the impurity bands with the result that measured DF and HF absorptions will reflect a greater proportion of all impurities rather than being selective (as implied by the data in Table 1). For instance, there will be a significant contribution to DF laser losses from the H_2O band because the magnitude of the wing of the H_2O band at 3.5 μm (lower end of 3.5 to 4.0 μm DF laser output) is about 20% of that at 2.8 μm. Even considering this multiline output, however, the DF and HF absorptions should not be equal after exposure to H_2O or D_2O.

E. CONCLUSIONS

The study of DF and HF laser absorption by KCl and CaF_2 selectively exposed to water and hydrocarbons has shown that the surface absorption increases with long exposures to the contaminant. In general, the 3.8 and 2.8 μm absorption increases by about the same amount for water or hydrocarbons. This is not readily explained in terms of the frequency and width of the impurity bands.

SECTION 3

DELAYED FAILURE TESTING OF COATED AND UNCOATED CaF_2 AND SrF_2

A. INTRODUCTION

The strength of transparent materials is an important parameter in the selection of reliable infrared laser window materials. It has been found that hard materials, such as ZnSe and the alkaline earth fluorides, fail mechanically at flaws and imperfections originating at the surface. The ultimate strength of an optical component is thus often limited by its surface characteristics. Although careful polishing techniques can be used to improve the overall mechanical strength, it would be desirable to investigate other methods of surface hardening in the hope of possibly increasing and stabilizing the surface strength of transparent materials.

The method selected for our surface hardening investigation is the use of certain optical coating materials. In particular, we decided to use sapphire (Al_2O_3) single-layer coatings on SrF_2 and CaF_2 as a means of studying the effect of coating on hardness. Since this coating material also has resonably good transparency at 3.8 μm, it could easily be incorporated into multilayer dielectric stacks used as AR coatings if the Al_2O_3 proved to harden materials.

The mechanical testing of the samples involved delayed failure testing. In this test, the failure time is measured as a function of applied stress. These methods can provide information about safe lifetimes for materials as well as the more conventional data on strength. In real life situations, delayed failure analysis can be a meaningful type of analysis as it provides information useful in predicting the reliability of window materials, information that cannot be obtained from yield strength measurements alone. The delayed failure testing was done at NRL in collaboration with Dr. Steve Freiman.

B. EXPERIMENTAL TECHNIQUES

A series of CaF_2 and SrF_2 rectangular parallelepipeds (1/8 in. x 1/4 in. x 1 in.) were cut and polished. Approximately 10 bars cut from polycrystalline SrF_2 (grown and forged in our laboratory) were coated on one side (1/4 in. x 1 in. side) with Al_2O_3 (about 2 μm thick); another 10 bars of the same material were left uncoated. A similar series of coated and uncoated samples was also made from single-crystal CaF_2 (grown in our laboratory). These samples were then sent to NRL for delayed failure testing.

C. RESULTS AND DISCUSSION

The first series of tests were performed on the SrF_2 samples. Lacking definitive data on the ultimate strength of these particular samples, we decided, based on previous work with polycrystalline SrF_2, to use a static load of 7000 $lb/in.^2$ for testing failure. Table 2 lists the results for the coated and uncoated samples of SrF_2. These results show that the static load was too high, which caused many of the samples to break during loading. From the range of stresses required to break the samples, an average stress $\bar{\sigma}$ can be calculated. For the uncoated SrF_2, $\bar{\sigma}$ is 5780 ± 1530 $lb/in.^2$; for the coated SrF_2, $\bar{\sigma}$ is 5670 ± 1110 $lb/in.^2$ These numbers not only clearly indicate the large scatter in the strength values, but they also imply that this material is not as strong as expected. Since polycrystalline SrF_2 is typically 7000 to 10,000 psi in ultimate strength, this particular material must be of poorer quality. Unfortunately, as Table 2 shows, it is not possible to draw any conclusions regarding hardening of the surface by coating with Al_2O_3 because of the wide range of strength values.

The delayed failure testing for the single-crystal CaF_2 was unsuccessful because the static load (6000 $lb/in.^2$) used was too low. Five uncoated bars of CaF_2 were tested from 200 to 2000 hr at 6000 $lb/in.^2$ and none failed (broke). The static load was then increased to 7000 $lb/in.^2$ and again none broke for testing times to 1600 hr. Increasing

Table 2. Delayed Failure in Coated (Al_2O_3) and Uncoated Polycrystalline SrF_2

Coating	Sample No.	Stress σ, lb/in.^{2}	Time to Failure, sec
None	1	7000	1080
	2	7000	5
	3	7000	9
	4	7000	340
	5	6120	[a]
	6	3140	[a]
	7	4471	[a]
	8	4520	[a]
Al_2O_3	1	3740	540
	2	7400	[a]
	3	5900	[a]
	4	5610	[a]
	5	5000	[a]
	6	5940	[a]
	7	6080	10440

[a] Broke during loading; breaking load indicated under σ.

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the load to 8000 lb/in.^{2} resulted in only one failure (at 0.2 hr), and the testing was terminated. Again, as was the case for SrF_2, no meaningful results were produced during these tests because the initial static load was insufficient. The coated CaF_2 samples were not tested because Steve Freiman left NRL and because, with the end of this contract, testing was suspended.

The basic question addressed by this portion of the program thus remains unanswered. To determine whether selective coatings such as Al_2O_3 harden transparent material requires additional testing on, for example, the remaining CaF_2 samples. It may be possible to measure failure on these samples at a future date in related on-going research programs.

REFERENCES

1. Hass, M. and Bendow, B., "Residual Absorption in Infrared Materials," *Appl. Opt.* 16:2882 (1977).

2. Holm, R.T. and Palik, E.D., "Thin-Film Absorption Coefficients by Attenuated-Total-Reflection Spectroscopy," *Appl. Opt.* 17:394 (1978).

3. Palik, E.D., Gibson, J.W., Holm, R.T., Hass, M., Braunstein, M., and Garcia, B., "Infrared Characterization of Surfaces and Coatings by Internal-Reflection Spectroscopy, *Appl. Opt.* 17:1776 (1978).

4. See, for example, *Infrared Spectroscopy in Surface Chemistry*, M.L. Hair, Marcel Dekker, New York, N.Y. (1967).

5. Duthler, C.J., "Extrinsic Absorption in 10.6 μm-Laser-Window Materials Due to Molecular-Ion Impurities," *J. Appl. Phys.* 45:2668 (1974).

6. Flannery, M. and Sparks, M., "Extrinsic Absorption in Infrared Laser-Window Materials," in Laser Induced Damage in Optical Materials: 1977, NBS Special Publication No. 509, ed. by A.J. Glass and A.H. Guenther, p. 5 (1977).

7. Hass, M., Davisson, J.W., Klein, P.H., and Boyer, L.L., "Infrared Absorption in Low-Loss KCl Single Crystals Near 10.6 μm," *J. Appl. Phys.* 45:3959 (1974).

8. Rosenstock, H.B., Hass, M., Gregory, D.A., and Harringston, J.A., "Analysis of Laser Calorimetric Data," *Appl. Opt.* 16:2837 (1977).

9. Barraclough, P.B., and Hall, P.G., "Adsorption of Water Vapor by Calcium Fluoride, Barium Fluoride, and Lead Fluoride," *J. Chem. Soc. Faraday Trans.* 171:2266 (1975).

10. Sparks, M., private communication.

APPENDIX

The reports, publications, and presentations produced during the three years of this research program are summarized below (in chronological order).

1. Braunstein, A., Braunstein, M., Rudisill, J., Harrington, J.A., and Gregory, D.A., "Coating Materials for Chemical Laser Windows," in Proceedings of the Fifth Conference on Infrared Laser Window Materials, sponsored by DARPA, p. 347 February 1976.

2. Holm, R.T., Palik, E.D., Gibson, J.W., Braunstein, M., and Garcia, B., "Evaluation of Thin Film Coatings by Attenuated Total Reflection," presented at Topical Meeting on Optical Phenomena in Infrared Materials, Dec. 1-3, 1976, Annapolis, Maryland. Abstracts in *J. Opt. Soc. Am.* 67:245 (1977).

3. Holm, R.T., Palik, E.D., Gibson, J.W., Braunstein, M., and Garcia, B., "Attenuated Total Reflection Measurements of Absorption in Thin Film Coatings," *Bull. Am. Phys. Soc.* 22:295 (1977).

4. Palik, E.D., Gibson, J.W., Holm, R.T., Hass, M., Braunstein, M., and Garcia, B., "Infrared Characterization of Surfaces and Coatings by Internal Reflection Spectroscopy," *Appl. Opt.* 17:1776 (1978).

5. Hass, M., and Harrington, J.A., "HF and DF Window Absorption," in proceedings of the High Power Laser Optical Components and Component Materials, sponsored by DARPA, p. 157, Dec. 1977.

6. Hass, M., Rosenstock, H., Davisson, J., and Harrington, J.A., "Surface Absorption by Laser Calorimetry," ibid, p. 211.

7. Harrington, J.A., "Surface Absorption in KCl and CaF_2 at DF and HF Laser Wavelengths," to be published.