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**LOW LOSS WINDOW MATERIALS FOR
CHEMICAL LASERS**

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Calorimetric measurements of the optical absorption coefficient at chemical laser frequencies will be reported on single and polycrystalline alkaline earth fluorides and alkali halides, single crystal magnesium oxide, sapphire, magnesium fluoride, strontium titanate, and other materials. Infrared spectrometer data on the absorption coefficient as a function of frequency for most of the materials studied are presented. As in past work, these data serve to indicate the value of the absorption coefficients expected in the HF-DF frequency regime. The infrared scans also reveal impurity structure in a few oxide materials in this same region.

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LOW LOSS WINDOW MATERIALS FOR CHEMICAL LASERS

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PREFACE

This report describes work on low loss window materials for chemical lasers performed during the period 10 July 1974 to 9 January 1975 on Contract No. DAAK01-74-C-0437, ARPA Order 2614. Participating in the research were, in addition to the principle investigator James A. Harrington, Don Gregory, William Otto, Ben Ferguson, and Lain Kan.

SUMMARY

The increasing interest and importance of chemical lasers has led to a demand for further materials studies at DF and HF chemical laser frequencies. In order to meet this demand a small cw chemical laser has been built for calorimetric measurements of the absorption coefficient. A wide variety of low loss materials has been studied at DF (3.8 microns) and HF (2.7 microns) frequencies. In conjunction with the absorption measurements, chemical cleaning and polishing techniques have been developed and applied to some materials to determine their effectiveness in minimizing surface absorption.

Calorimetric measurements of the optical absorption coefficient at chemical laser frequencies will be reported on single and polycrystalline alkaline earth fluorides and alkali halides, single crystal magnesium oxide, sapphire, magnesium fluoride, strontium titanate, and other materials. The measured absorption coefficients at these frequencies have been found to essentially agree with the intrinsic values in the case of those materials whose absorption is dominated by multiphonon processes (e.g. in sapphire, strontium titanate, etc.) and to vary widely for those materials whose absorption is limited by extrinsic processes (e.g. alkali halides and alkaline earth fluorides). In the latter case it is suspected that the presence of OH⁻ ion impurities, which produce strong absorptions at HF frequencies, may account for some of the high values of the absorption coefficient.

For reference purposes, [✓]infrared spectrometer data on the absorption coefficient as a function of frequency for most of the materials studied are presented. As in past work, these data serve to indicate the value of the absorption coefficients expected in the HF-DF frequency regime. The infrared scans also reveal impurity structure in a few oxide materials in this same region.

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I. INTRODUCTION

The primary objective of this research program is to investigate the optical properties of materials which are candidates for service as low loss windows on DF and HF chemical lasers. During the past six months, measurements of the optical absorption coefficient have been carried out on a large number of solids at DF (3.8 microns) and HF (2.7 microns) frequencies using cw chemical laser calorimetry. These studies, which include results for many state-of-the-art materials, allow us for the first time to begin to systematically evaluate, in terms of the absorption coefficient, the potential of many materials as windows at chemical laser frequencies.

A survey¹ of optical properties of materials indicates that there are many substances, based on absorption coefficient alone, which would be good candidates for DF and HF laser windows. In reviewing these potential materials it is apparent that there are two categories of materials. There are those like the alkali halides and alkaline earth fluorides which would be expected to have a very small absorption coefficient β at chemical laser wavelengths due to their small intrinsic absorption. That is, if one extrapolates, following the approach of Deutsch², a plot of $\log \beta$ versus frequency to the laser frequency one obtains the value of the intrinsic (multiphonon) contribution to the total absorption. For the materials mentioned above this contribution is usually many orders of magnitude below what is actually measured. As an example,

the absorption coefficient of SrF_2 predicted by the extrapolation of $\log \beta$ vs. ω to 3.8 microns is $5.1 \times 10^{-9} \text{ cm}^{-1}$. The other alkali halides and alkaline earth fluorides exhibit β values which are similarly orders of magnitude below the measured β values. Therefore in this category the measured absorption in the DF to HF frequency regime will be due to extrinsic (surface, impurities, imperfections, etc.) processes. The other category is those substances for which the absorption is more obviously intrinsic. These include Al_2O_3 , MgO , SrTiO_3 , and YttraloxTM Ceramic. In these cases the absorption is expected to be limited by multiphonon processes and the measured values should lie near the $\log \beta$ versus ω plots.

During the course of routine measurements of the optical absorption it became evident, especially when several unexpected results occurred, that one is faced with a slightly different situation at DF-HF frequencies than at CO_2 or even CO wavelengths. On one hand, it was found that almost all materials had higher values of β at 2.7 microns than at 3.8 microns. This result, which is clearly contrary to intrinsic or even "normal" (i.e. flat response) extrinsic behavior, is probably due to absorption by OH^- ions in or on the surface of the samples. In addition, it was noticed that in some samples the surface absorption was abnormally high. It is thought that this strong surface contribution to the total absorption is most likely due to organic materials used in surface finishing. This effect along with results of all absorption measurements

at HF and DF frequencies is discussed in Section III.

II. EXPERIMENTAL TECHNIQUES AND PROCEDURES

The experimental technique of laser calorimetry used to measure the small absorption has been well documented. Our method follows closely that described by Hass, et al.³. One aspect of particular interest is the small cw chemical laser of our own construction used for the measurements. The laser is of the SF₆ variety, delivering from 5 to 10 watts of cw multiline HF power and about 5 watts of cw multiline DF power. The device can be safely and easily operated by one person. The frequency dependence of the absorption coefficient was obtained for several of the samples at room temperature using a Beckman IR-12 infrared spectrometer.

Samples suitable for calorimetric measurements were received from many sources (cf. Tables 1-3). When the samples were obtained with polished surfaces, they were always measured first in the as-received condition. This was done in order to furnish the donating laboratory a value of β which would not only reflect the quality of the material but also the quality of the surface finish provided. In some cases it was then necessary to clean the surfaces and/or repolish the samples to minimize surface contamination and reduce the absorption coefficient. In those instances where samples were received unpolished, standard mechanical polishing techniques were employed by us to finish the surface. In the case of one

sample of CaF_2 , a chemical polish of our own composition⁴ was employed to determine the effect of chemical polishing on β .

III. EXPERIMENTAL RESULTS

A. Alkaline Earth Fluorides

Alkaline earth fluorides are a class of cubic ionic solids showing great promise as laser window materials. Several laboratories are engaged in producing low loss, high strength windows from CaF_2 , BaF_2 and SrF_2 hosts and some of these newest materials have been obtained for evaluation. As growth methods and fabrication procedures improve, it is anticipated that more samples will become available for measurement.

Table 1 lists the β values for both single and polycrystal alkaline earth fluorides measured to date. This table also lists the source of supply and, for some samples, lists the value of β measured with a CO laser calorimeter.⁵

In conjunction with this data it is useful for reference to compare our calorimetric data to the β vs. frequency data obtained from infrared spectroscopy and, in some cases, spectral emittance measurements.⁶ In Figures 1-3, $\log \beta$ is plotted versus the energy (cm^{-1}) over the range accessible to dual beam spectroscopy. The solid lines are an average of the experimental results obtained from Deutsch² while the dotted lines are an extrapolated continuation of this data. The calorimetric data are plotted as points or, in those cases where more than one sample

TABLE 1
Absorption Coefficient for Alkaline Earth Fluorides
at Chemical Laser Frequencies

Sample		Source	Absorption Coefficient (cm^{-1})		
P-Polycrystal	S-Single Crystal		Deutsch CO(5.25 μm)	Chemical Laser DF(3.8 μm)	Calorimetry HF(2.7 μm)
CaF ₂	(P)	Harshaw	8.0×10^{-4}	5.42×10^{-3}	3.67×10^{-3}
CaF ₂	(S)	Harshaw	-	2.67×10^{-4}	5.21×10^{-3}
CaF ₂	(S)	Optovac	-	5.9×10^{-4}	7.8×10^{-4}
CaF ₂	(P)	Raytheon	-	5.18×10^{-3}	4.56×10^{-3}
CaF ₂	(P)	Raytheon VHP-262	5.3×10^{-4}	6×10^{-4}	1.48×10^{-3}
CaF ₂	(P)	Raytheon VHP-264	4.9×10^{-4}	6×10^{-4}	-
BaF ₂	(P)	Harshaw	1.2×10^{-3}	3.66×10^{-3}	4.42×10^{-3}
BaF ₂	(S)	Optovac	-	2.0×10^{-3}	1.8×10^{-3}
SrF ₂	(P)	Harshaw	1.4×10^{-4}	1.25×10^{-3}	2.22×10^{-3}
SrF ₂	(S)	Optovac	-	9.48×10^{-4}	1.5×10^{-3}
SrF ₂	(P)	Raytheon	-	7.1×10^{-4}	1.5×10^{-3}

was available, as a range of values as indicated in Table 1.
The spectral emittance results are discussed in Section 4.

B. Alkali Halides, Oxides, and Miscellaneous Materials

At chemical laser frequencies, an important class of window materials is the oxides. Table 2 shows that the

Table 2
Absorption Coefficient for Various Materials
at Chemical Laser Frequencies

Sample	Source	Absorption Coefficient (cm^{-1})	
		Chemical Laser DF(3.8 μm)	Calorimetry HF(2.7 μm)
NaF	Optovac	7.04×10^{-4}	8.23×10^{-4}
MgF ₂	Optovac	4.66×10^{-4}	8.61×10^{-4}
MgO	Norton	5.43×10^{-3}	4.02×10^{-2}
SrTiO ₃	NL Industries	1.02×10^{-2}	5.5×10^{-3}
SrTiO ₃	NL Industries	2.98×10^{-2}	7.36×10^{-3}
Al ₂ O ₃	Crystal Systems	3.05×10^{-2}	1.48×10^{-3}
Al ₂ O ₃	AMMRC	3.38×10^{-2}	4×10^{-3}
Yttralox	GE	6.26×10^{-3}	6.02×10^{-3}
KCl	Oklahoma State Univ.	3.12×10^{-4}	1.22×10^{-3}
NaCl (S)	Harshaw	-	1.64×10^{-3}
NaCl (P)	Harshaw	-	1.82×10^{-3}
ZnSe (CVD)	Raytheon	-	1.58×10^{-2}

various oxides do not always have as small an absorption coefficient as say the alkaline earth fluorides. They do, nevertheless, possess appealing mechanical properties which tend

to offset the higher values of β . Table 2 also lists β values for the alkali halides and ZnSe (obtained from Raytheon). Again infrared scans of the absorption versus frequency are given in Figures 4-9 for most of the crystals in Table 2. In all of these curves as in Figures 1-3, the solid portion corresponds to actual data while the dotted line is the extrapolation of this data. The IR data was taken from published values when there was essentially no disagreement between the literature values and our results. In many cases, especially those involving the less widely studied materials like YttraloxTM and other oxides, the IR results were taken in our laboratory using the Beckman IR-12. In Figure 7 (MgO) and Figure 8 (YttraloxTM) the bands between the DF and HF frequencies represent observed impurity bands.

IV. DISCUSSION

A. Alkaline Earth Fluorides

The alkaline earth fluorides are an increasingly important class of materials for chemical laser windows because of their potentially small absorption and other attractive physical properties. One can see from Figures 1-3 that the absorption at DF and HF wavelengths should be limited only by extrinsic processes and thus should be capable, through continually improving crystal growth and purification techniques, of reduction to very small values to at least the low 10^{-4} cm^{-1}

range. The calorimetric data reveal, however, that in most instances the values of β actually measured are far above the expected values for these materials. In part this is due to the state-of-the-art of these hosts; a situation that may be compared to the evolutionary process of the decrease in β in KCl at 10.6 microns. In addition to problems concerning the level of extrinsic absorption there still remain, however, several features peculiar to chemical laser frequencies that have been detected.

One such feature observed in almost all the data is the higher value of β at HF frequencies. It is believed that this is due to absorption by OH^- ions in or on the surface of the samples. It is well known that OH^- absorbs in ionic solids at selected frequencies within the HF laser frequency range. Measurements at these frequencies then can be an indicator of the OH^- content of the crystal. Future plans call for tunable HF calorimetry to get an improved estimate of the extent of this absorption.

In many of these samples it was very disquieting to find such high values of β at DF wavelengths for while it is possible to postulate the existence of OH^- and correspondingly high β values at HF wavelengths, it is difficult to extend this argument to 3.8 microns. Therefore a sample of Raytheon CaF_2 which had been measured at CO (5.2 microns) wavelengths and found to have a $\beta = 5 \times 10^{-4} \text{ cm}^{-1}$ was chemically cleaned after an initial measurement at 3.8 microns on the as-received sample.

The cleaning involved merely soaking in methanol followed by careful drying. It was found that after remeasuring the sample using the DF laser the initial $\beta = 2 \times 10^{-3} \text{ cm}^{-1}$ had fallen to $\beta = 6 \times 10^{-4} \text{ cm}^{-1}$ (the value shown in Table 1 for CaF_2 , Raytheon VHP-262 and VHP-264). This indicates the necessity of careful cleaning to remove organic matter used in finishing the sample's surface as organics absorb strongly in this region. This undoubtedly accounts for part of the discrepancy between the CO $\beta = 5 \times 10^{-4} \text{ cm}^{-1}$ and the DF $\beta = 6 \times 10^{-4} \text{ cm}^{-1}$. In another case, the Optovac single crystal CaF_2 was initially measured at DF frequencies with a resulting $\beta = 8.4 \times 10^{-4} \text{ cm}^{-1}$. This sample was then chemically polished using an acid solution of our own composition⁴. On remeasuring using a DF laser β was observed to have been lowered to $5.9 \times 10^{-4} \text{ cm}^{-1}$ (value in Table 1). Both of these examples indicate surface contamination is a significant factor in many of these materials. Future plans include a more detailed investigation of this surface absorption problem.

The data in Figures 1-3 include results from spectral emittance measurements⁶ on the Harshaw Polytran samples taken at 373 K. At the longer wavelengths these data lie above Deutsch's curves. This is due to the temperature dependence of the absorption coefficient⁷. The "tailing up" of the emittance data above 2000 cm^{-1} is most likely due to scattering of light from the sample holder. These data, therefore, do not necessarily represent the true value of β for

frequencies higher than 2000 cm^{-1} .

B. Alkali Halides, Oxides, and Miscellaneous Materials

Many of the comments made concerning results for the alkaline earth fluorides pertain directly to the results for these materials. In almost every case, with the exception of Al_2O_3 and SrTiO_3 , the values of β at HF wavelengths are greater than those at DF wavelengths. This is especially true for the extrinsically limited materials like the alkali halides. Here again it is presumed that absorption by OH^- ions is in large measure responsible for this feature in the data. It is also quite likely that surface contamination contributes some to the β values at both DF and HF frequencies. However, no systematic chemical cleaning or polishing before-and-after tests have yet been performed using these samples as was done for the alkaline earth fluorides.

The data for the oxides in Figures 6-8 present some interesting and unexpected results. For sapphire, Figure 6, it is noticed that the DF value of β falls above the measured infrared spectrometer data. A possible explanation of this is that the chemical laser in multiline operation puts out all frequencies present between 3.5 and 4.0 microns. Thus the point plotted at 3.8 microns represents an average value over the range of frequencies. A more detailed study employing tunable DF laser calorimeter is in progress to obtain more exact data.

Figures 7 and 8 exhibit impurity bands observed in MgO and YttraloxTM between the HF and DF frequencies with the infrared spectrometer. It is clear that this extrinsic absorption accounts for the higher than expected β values. Both MgO and YttraloxTM (90% Y_2O_3 and 10% ThO_4)⁸ have potentially lower β 's than Al_2O_3 while retaining many of the desirable mechanical properties of oxides in general. Therefore it is important to learn the exact nature of this extrinsic absorption. At the moment it is felt that the possible containmant is OH^- . Additional samples are being procurred to help answer some of the questions regarding these absorption bands.

V. CONCLUSIONS

An initial investigation has been made of the optical absorption in materials that are candidates for service as DF and HF chemical laser windows. The primary aim has been to measure β using chemical laser calorimetry for a wide variety of materials. The number of different samples measured included some, such as the oxides, which have rather high values of β . The oxides will continue to be investigated with the hope that purer materials will be found which are free of absorption bands in the HF-DF region and thus have more nearly intrinsic β 's. For example, both MgO and YttraloxTM should have intrinsic β 's in the 10^{-4} cm^{-1} range rather than

the β 's in the 10^{-3}cm^{-1} currently measured. Such materials would then provide the very desirable combination of good mechanical and optical properties.

Future work will emphasize the alkaline earth fluorides as these materials are receiving increasing attention as prime candidates for windows. It is expected that state-of-the-art samples will continue to be received from various national laboratories engaged in high purity alkaline earth fluoride crystal growth programs and that these samples will improve in quality as time goes on. Measurements to date indicate a wide range of β values. In the future these will undoubtedly approach the low 10^{-4}cm^{-1} range on a consistent basis. Throughout the next six month period data on the new samples will, as usual, be fed back to the supplier for use in evaluating their crystal growth programs.

Finally, more work will be done on chemical cleaning and polishes to determine their effect on the reduction of the optical absorption. It is anticipated that the institution of even the most basic cleaning procedures will yield a systematic reduction in the surface absorption.

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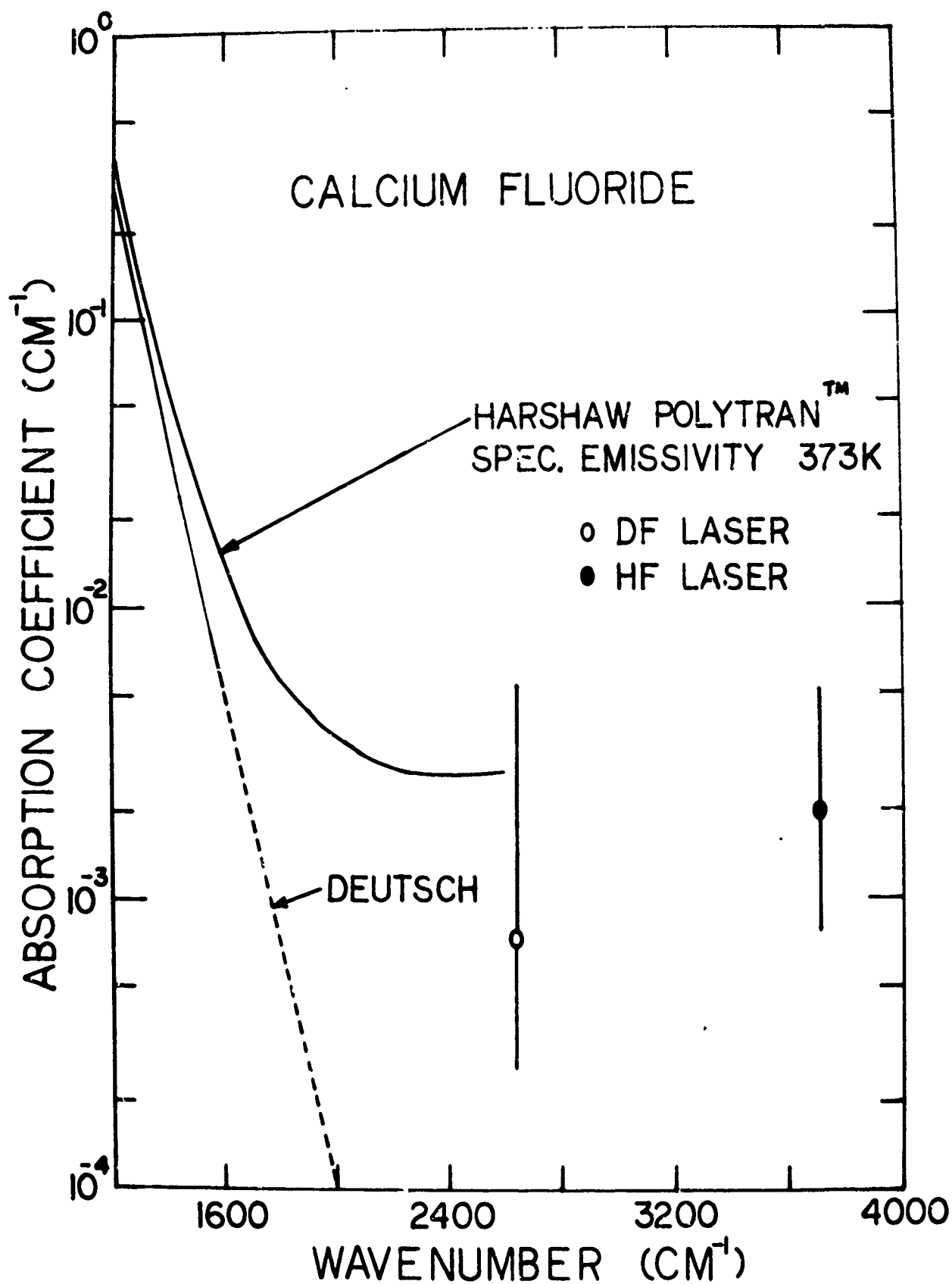


Figure 1 - Absorption coefficient of calcium fluoride.
versus frequency.

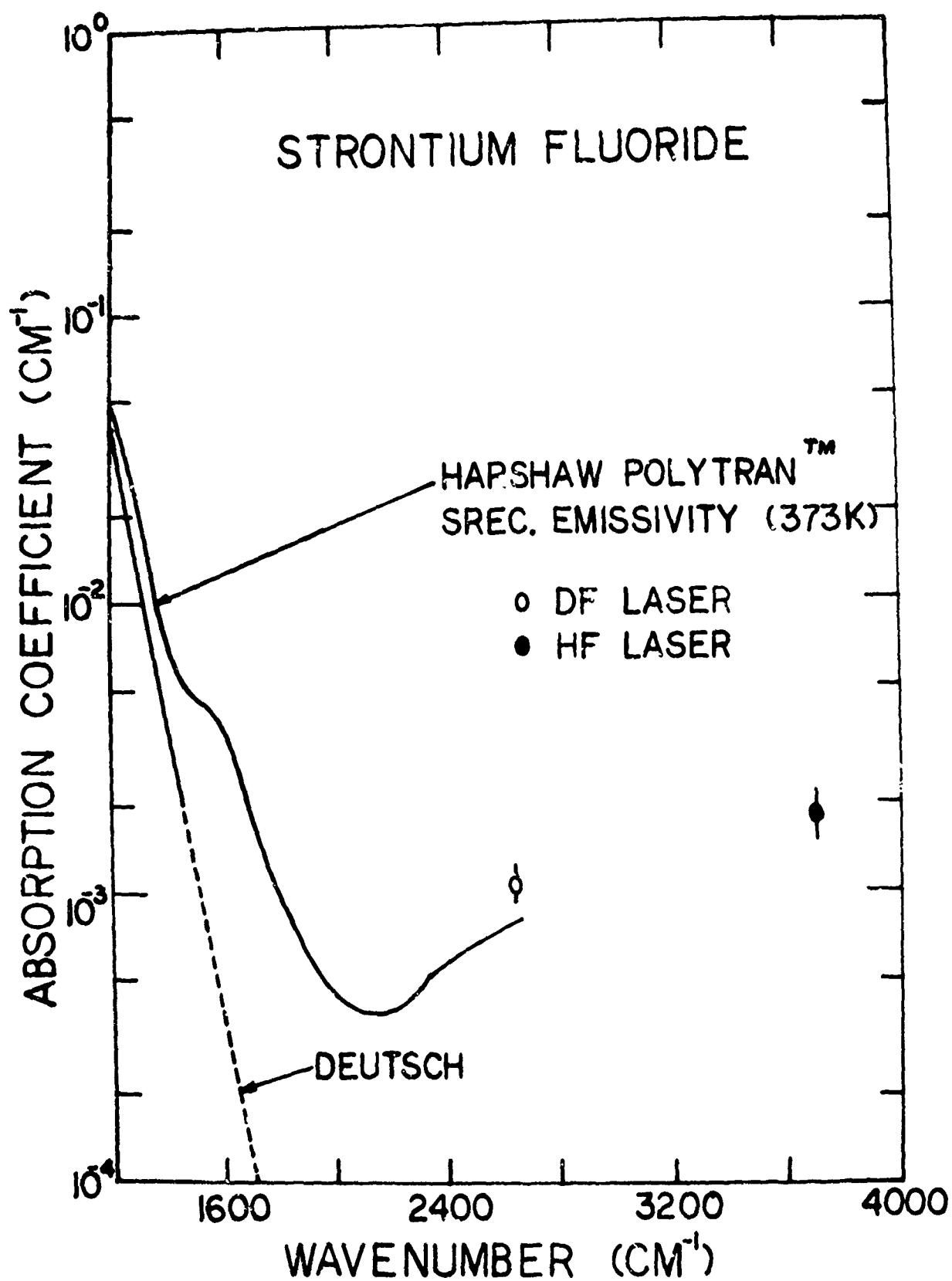


Figure 2 - Absorption coefficient of strontium fluoride versus frequency.

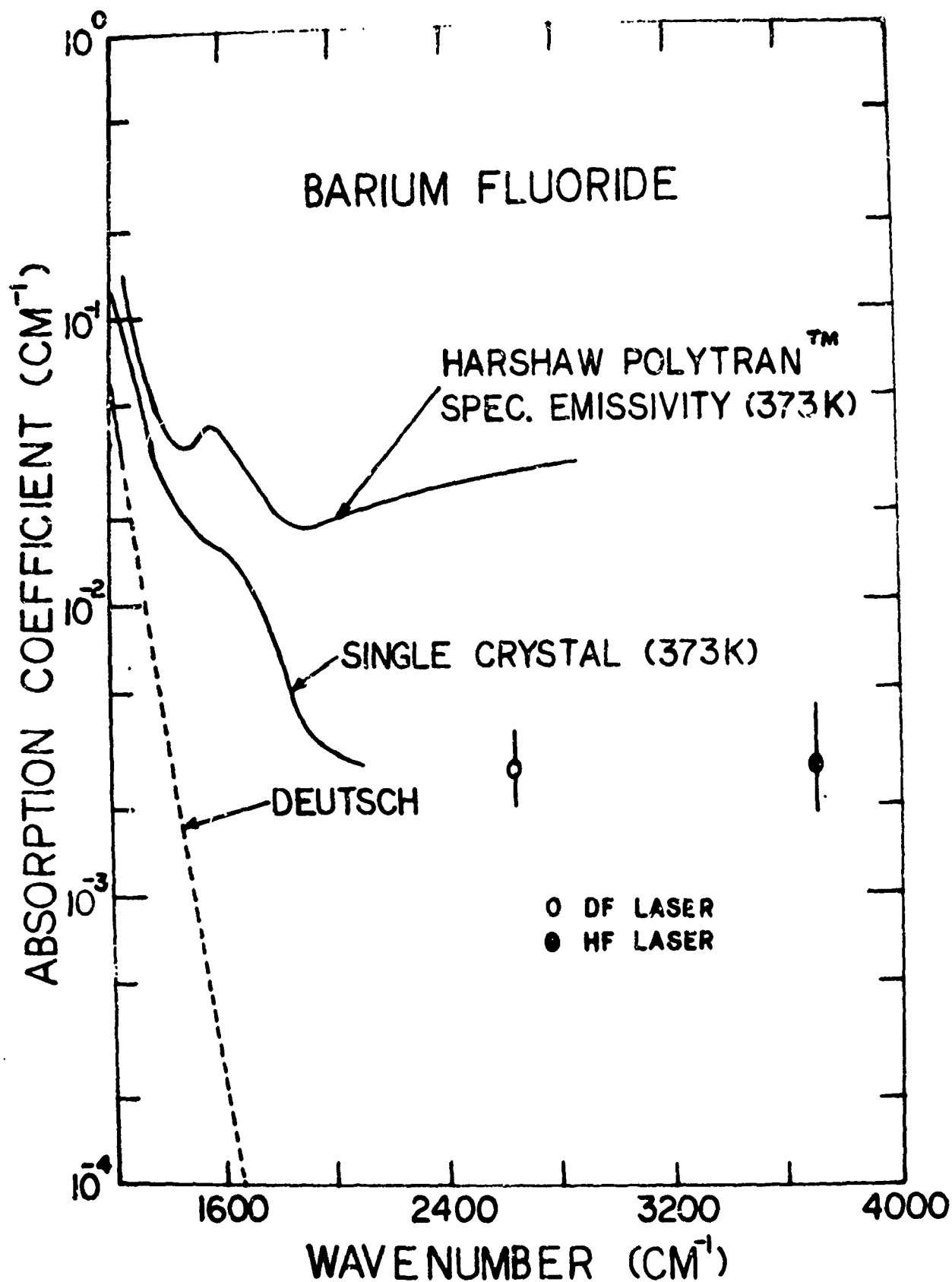


Figure 3 - Absorption coefficient of barium fluoride versus frequency.

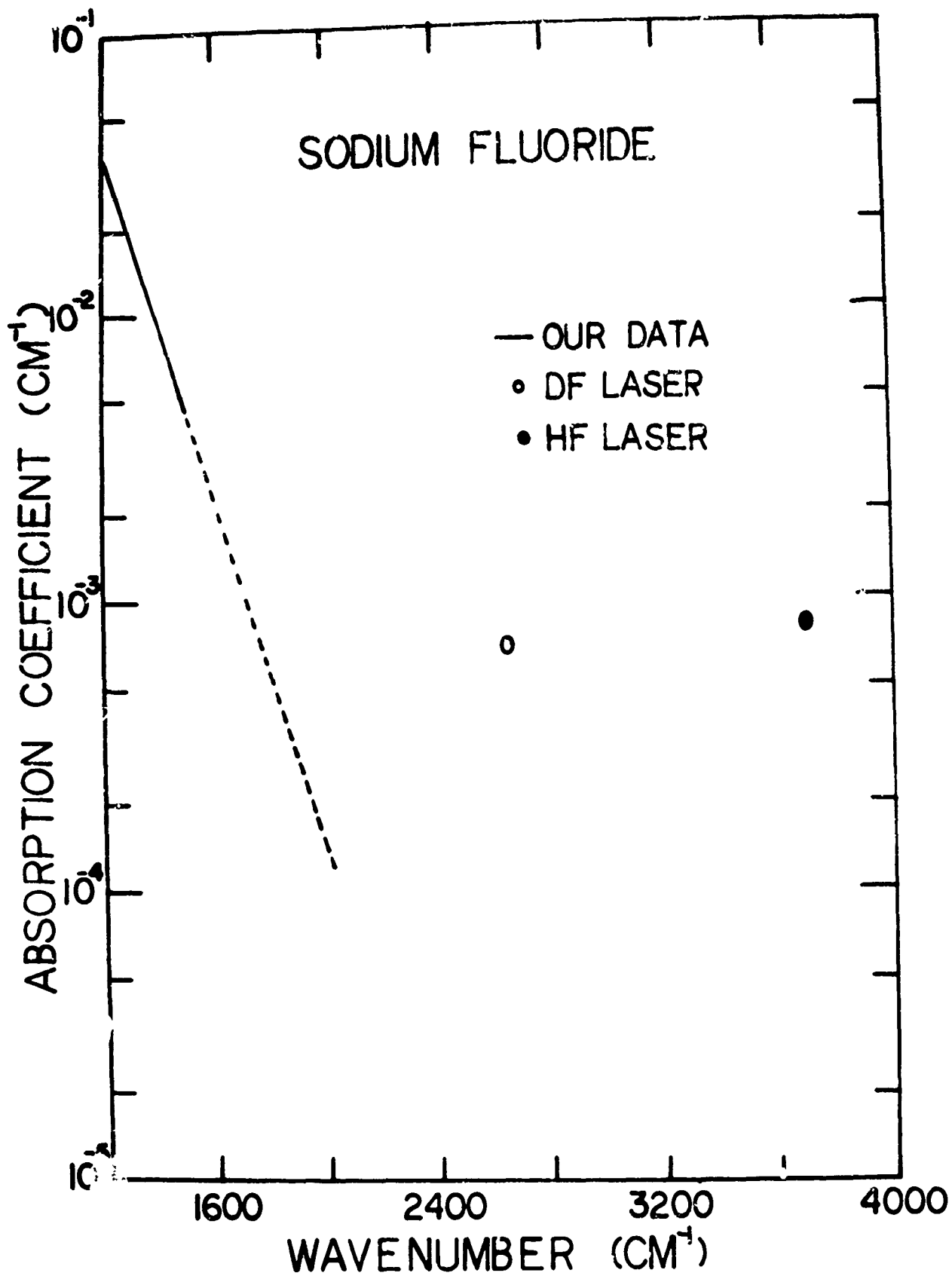


Figure 4 - Absorption coefficient of sodium fluoride versus frequency.

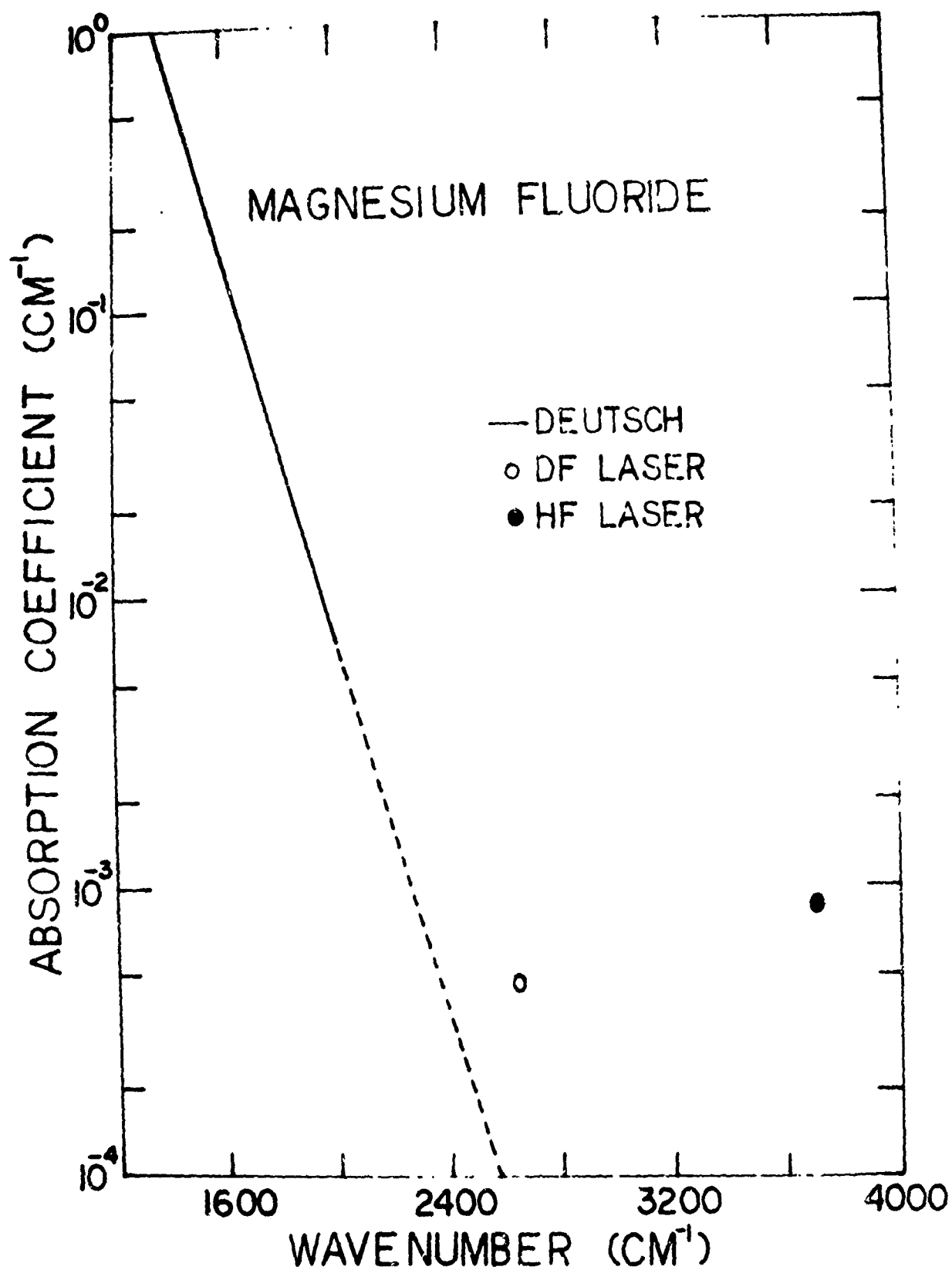


Figure 5 - Absorption coefficient of magnesium fluoride versus frequency.

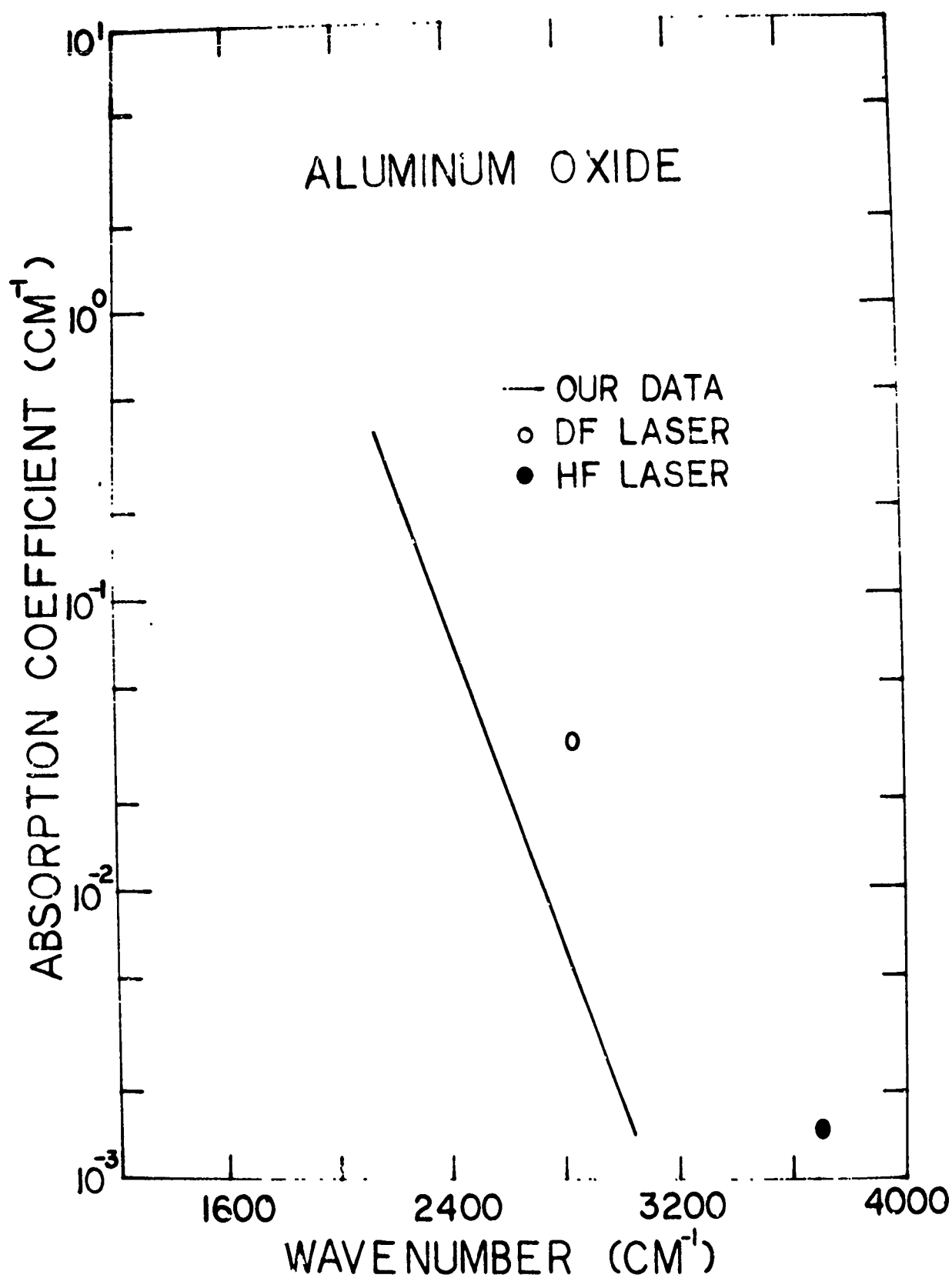


Figure 6 - Absorption coefficient of aluminum oxide versus frequency.

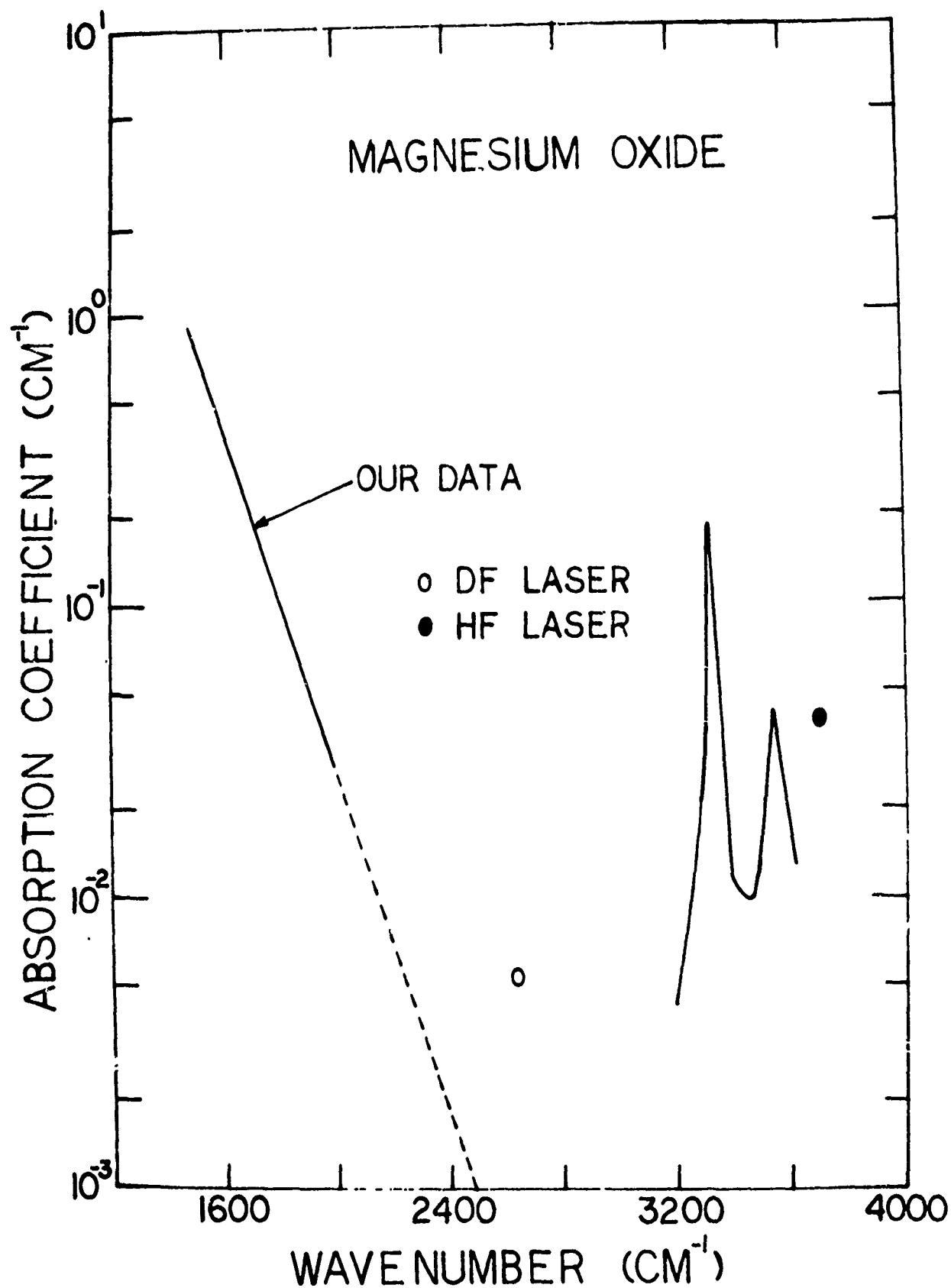


Figure 7 - Absorption coefficient of magnesium oxide versus frequency.

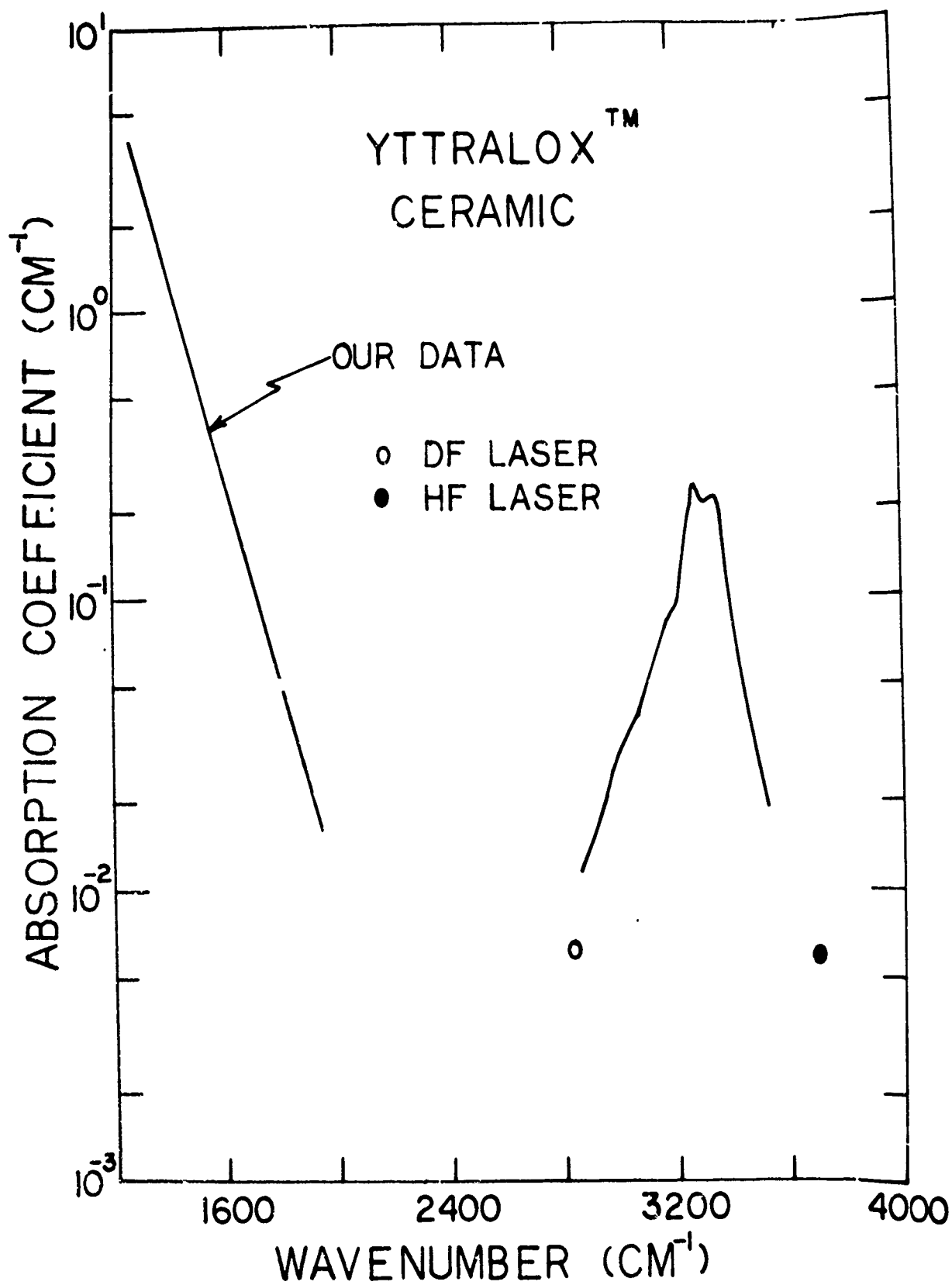


Figure 8 - Absorption coefficient of YttraloxTM ceramic versus frequency.

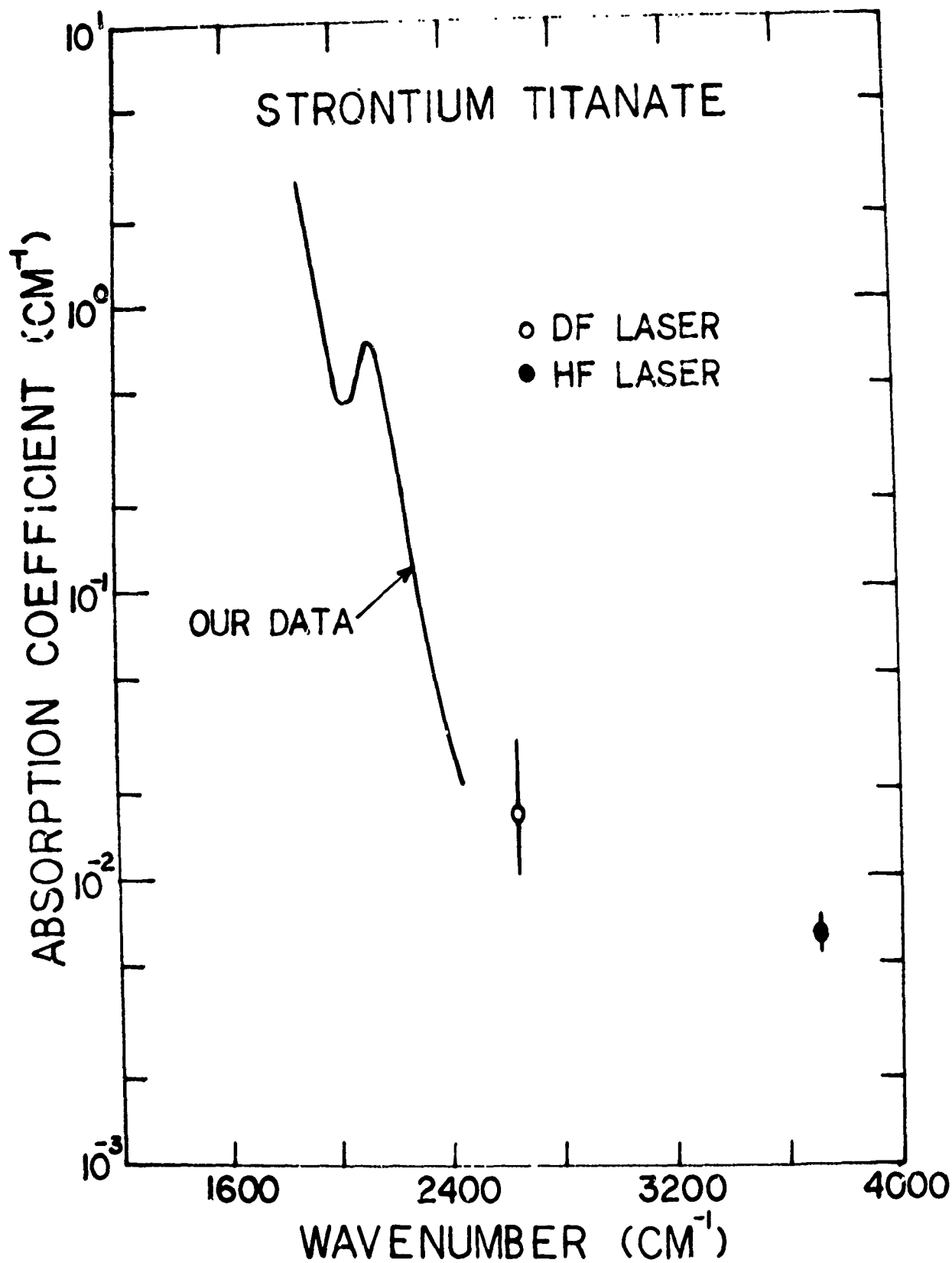


Figure 9 - Absorption coefficient of strontium titanate versus frequency.