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GODDARD SPACE FLIGHT CENTER
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A report dealing with a new theory of the shape of pressure induced spectra with an application to the far infrared spectrum of eH_2 at 77K is appended.

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ABSTRACT

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FOREWORD

The work reported here was supported by the National Aeronautics and Space Administration, Goddard Space Flight Center through Contract No. NAS5-20820 with Mr. V. Kunde serving as the program monitor. Dr. George Birnbaum was the Principal Investigator of the program and was assisted in the experimental work by Mr. R. K. Horne.

The theoretical work performed in collaboration with Dr. E. R. Cohen was supported through corporate IR&D funding except for the application of the theory to H_2 which was supported through Contract No. NAS5-20820.

I. INTRODUCTION

In a previous investigation of the far infrared spectrum of eH_2 and an eH_2-He mixture, the absorption coefficient was determined in the region 10 to 600 cm^{-1} at 77, 195, and 293K.[1] The present investigation was undertaken to delineate the high frequency side of the S(1) line at 600 cm^{-1} by extending the measurements to 900 cm^{-1}. However, because the previous measurements in the region 500 to 600 cm^{-1} were inaccurate, the absorption coefficient in this region was remeasured. We have also determined the spectrum of nH_2 at 77K in the region 25 to 490 cm^{-1} since the translational band has been determined previously only to frequencies no lower than 50 cm^{-1} where the accuracy was particularly poor.[2] In addition we wished to verify what appeared to be a substantial difference between the shape of the translational band of nH_2 and eH_2 at 77K where it is relatively well resolved from the S(0) rotational line at 370 cm^{-1}.

To analyze the spectra obtained here and to calculate opacities of planetary atmospheres, it is necessary to have a theory of collision-induced line shapes. Such a theory is described in the report appended here and is applied to the far infrared spectrum of eH_2 at 77K.

2. EXPERIMENTAL CONSIDERATIONS

The spectra were obtained with the far infrared spectrometer[3] and dual beaming unit described previously.[1] However, to operate the equipment above 600 cm^{-1} several changes had to be made. The high density polyethylene windows terminating the 3.0m long gas cells rapidly become completely absorbing above 600 cm^{-1} due to a very intense band in the vicinity of 720 cm^{-1}. Consequently, these windows were replaced by KRS5 windows with a transmission coefficient of roughly 60 percent in the region 500 to 1000 cm^{-1}. This coefficient depends on the perfection of the surface polish and varied for the windows that were on hand. The windows, 2.5 cm diameter, one pair 1.3 cm thick and the other pair 0.78 cm thick, were sealed to the light pipes by a modification of the technique described in ref. 4. A low-temperature-resistant silicone rubber cement (MB0130-119) and primer (MB0125-050) developed by Space Division, Rockwell International, was used to bond the windows to the metal wall terminating the light pipe. To seal the light pipe from the external environment, a high density polyethylene disk 7.6 cm diameter was compressed between two flanges in the manner described previously.[1] In the present application, however, a 2.8 cm diameter hole was cut in the polyethylene disk to make room for the KRS5 window plus a brass ring concentric with the window. The latter prevented the polyethylene disk from exerting any pressure on the window and breaking its seal to the metal surface.

The KRS5 windows were used for the measurements at 195K. However, as the temperature of the gas cells were lowered to 77K, leaks developed through the window cement and neither cell could be pressurized. We decided to replace the

KRS5 windows with CsBr windows since we had learned from Harshaw that KRS5 may undergo a phase transition in the vicinity of 77K which makes it opaque. The CsBr windows were 2.5 cm diameter, 1.3 cm thick, and had a transmission coefficient close to 90 percent. Measurements with these windows were made at 293K at pressures as high as 60 atm in the test cell. The reference cell was filled with He at a much lower pressure to maintain a positive force on the window in order to ensure the seal. However, since the cells could be repeatedly filled with gas and evacuated, this precaution was not necessary although it was thought that the He might prevent the bath coolant from entering the cell in the event of a leak. On cooling the cells to 77K, the test cell was found to leak gas through the adhesive. However, it was possible to proceed with the absorption measurements by evacuating this cell and using it as the reference and using the other cell as the test cell. Evidently, the flow of the CsBr under 60 atmos pressure at 293K was great enough to weaken the seal to the point where it failed when cooled to 77K. The windows which were not subject to these pressures at 293K remained sealed at 77K.

For measurements on nH_2 at frequencies below 500 cm^{-1}, high density polyethylene windows were used to seal the gas cells.[1]

In order to operate at frequencies above 600 cm^{-1}, it was necessary to remove the black polyethylene film in front of the cooled bolometer because of its strong absorption in this spectral region. However, in order to avoid unnecessary heating of the bolometer as well as to provide additional filtering for the monochrometer, an OCLI filter L10928-9 with a band pass from roughly 450 to 900 cm^{-1} was mounted in front of the bolometer.

Another change that was made to improve the performance of the spectrometer was to install a 1.27 cm diameter light pipe following the exit slit. This replaced the 2.54 cm diameter light pipe coned down to 1.27 cm diameter that was used previously to increase the energy throughput of the spectrometer. To our surprise, the power at the detector increased by about a factor of four. The reason for this welcome increase was not determined.

Measurements in the region 500 to 900 cm^{-1} were made with a grating blazed at 15.0μ with 38.4 lines/mm ruled by PTR Optics. To filter the radiation from the source, an OCLI low pass filter No. L-13510-9 was used for frequencies from 450 to 700 cm^{-1}, and OCLI low pass filter No. L-07540-9 was used for frequencies from 700 to 900 cm^{-1}. These filters combined with the band pass filter in the bolometer provided very effective filtering. Since the absorption in H_2 at 600 cm^{-1} is relatively intense, a simple test for false radiation was provided by noting whether any energy was detected at sufficiently high pressure of H_2. Another test was provided by measuring the absorption coefficient as a function of density, since at the densities used the absorption is proportional to the square of the density, and at the power levels used, the bolometer response is linear in the applied power. In all cases the absorption coefficient was found to be accurately proportional to the density squared.

The grating was calibrated primarily with the lines at 698.7 and 906.7 cm^{-1} in a thin film of polystyrene,[5] and checked against a water vapor line at 525.98 cm^{-1} [6] and the Q-branch of the 15μ CO_2 band.[7] As a result of such calibrations we feel that the frequency is known to approximately ±0.5 cm^{-1} in the region 500-900 cm^{-1}.

At the beginning of this investigation, we noted that the grating angle at zero order (mirror angle) depended to a small extent on the slit width. This variation if uncorrected would have given an error in frequency measurements of 1 cm^{-1} or less. For this reason as well as one of convenience, the data were taken with only a few changes of slit width to maintain the spectral resolution in the range roughly 10 to 15 cm^{-1}. Since the diffraction angle is determined by subtracting the zero order angle from the grading angle, and the grating calibration was determined at the same slit widths, it was felt that no error in the frequency was introduced due to the variation of zero order angle with slit width. However, in the course of this investigation we decided to realign the monochrometer and recalibrate the grating. Although the realignment procedure removed the variation of zero order angle with slit width, we were pleased to note that the grating calibration was unchanged as were the absorption coefficients of H_2 that were remeasured.

Apart from the changes in the equipment that have been discussed, the experimental arrangement and procedure were identical with that used previously.[1] Even the gases were the same. However the nickel-silica powder (Apache 1, Air Products and Chemicals) used to produce eH_2 was placed in a stainless steel tube 60 cm long and 4mm ID rather than the 30 cm tube used previously. Since this change and measurements of the absorption coefficient of eH_2 at 77K and 600 cm^{-1} (near the peak of the S(1) line) for various reasonable flow rates of precooled H_2 through the catalyst produced no change in α/ρ_A^2 (cm^{-1} $amagat^{-2}$), we believe that the conversion of nH_2 to eH_2 to be complete.

3. EXPERIMENTAL RESULTS

The results for eH_2 at 293, 195, and 77K in the region 500 to 900 cm^{-1} are shown respectively in Figures 1 to 3 and for eH_2-He mixtures in Figures 4 to 6. The spectrum of nH_2 at 77K in the region 25 to 495 cm^{-1} is shown in Figure 7. The width of the S(1) line at 600 cm^{-1} ($J = 1 \rightarrow 3$) decreases with decreasing temperature in accordance with the decrease in the duration of collisions. The peak frequency is seen to increase from 598 to 608 cm^{-1} with increasing temperature and can be explained on the basis of our theory of collision induced line shape. The S(2) line whose Raman frequency is 814.4 cm^{-1} is seen in the H_2 and He-H_2 spectrum at 293 and 195K in the region roughly 780-880 cm^{-1}. As expected, the intensity of this feature decreases with decreasing temperature.

Detailed comparisons of the results in the region 500 to 600 cm^{-1} which overlapped the results obtained previously with a 20μ grating ruled with 23.9 lines/mm, showed that the latter gave values of $\alpha(\nu)/\rho_A{}^2$ consistently greater (by roughly 10 percent or less depending on the frequency) than the former. The many tests that were performed indicated that this discrepancy could arise from false radiation produced by scattering from the grating whose surface is of relatively poor quality. Measurements at 500 cm^{-1} and in some cases at lower frequencies showed that in this region the 15μ and 20μ gratings gave comparable results. However, since the latter was used to obtain the spectra in the region 320 to 500 cm^{-1} it was thought best to make further tests by installing a new 20μ grating ruled with 25.8 lines/mm by PTR optics with perhaps the best surface finish that we have seen to date. Measurements of $\alpha(\nu)/\rho_A{}^2$ on an eH_2-He mixture in the region 320 to 500 cm^{-1} gave results that were within experimental error similar to those obtained previously indicating that the old 20μ grating gave correct results in this region. We recommend then that the results in the region 500 to 600 cm^{-1} presented previously[1] (which were stated to be of lower accuracy) not be used and be replaced with those presented here.

Wherever possible comparison of the results obtained here were compared with those of other investigators. In the region 550 to 900 cm^{-1} our results for $\alpha(\nu)/\rho_A{}^2$ of H_2 are from 10 to 15 percent greater than those of Kiss et al.[8] On the other hand, in the region 700 to 900 cm^{-1} our results are from 5 to 10 percent less than those of MacTaggert and Hunt.[9] These discrepancies however are less than that between their data taken with a long cell (accurate data) and a shorter cell (less accurate data). As a check on the consistency of our results, we made measurements of $\alpha(\nu)/\rho_A{}^2$ on H_2 at 293K in the region 550 to 900 cm^{-1} with the 3 m cells terminated first by KRS5 and later by CsBr windows. The two sets of data agreed within several percent as did a similar comparison for eH_2 at 195K.

Our results for nH_2 at 77K and those of Bosomworth and Gush[2] agree on the average to within about 5 percent in the region 150 to 450 cm^{-1}. The agreement between 50 to 150 cm^{-1} becomes poor particularly at frequencies near 50 cm^{-1} where the scatter in their data[2] is severe. Their translational spectrum for nH_2 at 77K (the region 0 to 50 cm^{-1} was extrapolated since no data were obtained here) and the spectrum obtained here peak at quite different frequencies, the former apparently in the vicinity of 50 cm^{-1} and the latter at about 85 cm^{-1}. These results are to be compared with the translational band of eH_2 at 77K which peaks in the vicinity of 100 cm^{-1}.

The reason for the diagreement among the experimental results of the investigations cited here as well as previously[1] is not clear. In the course of our measurements, however, we found that the transmission coefficient of a gas cell filled with He varies in general to an extent depending on the pressure of He. This may be due to a slight motion of the window, but more likely to the extrusion of window material into the light pipe as a result of the pressure. Because of this effect, we always measured the transmission of the test cell filled with the gas under study relative to the transmission of the same cell filled with He to the same pressure. Unless this is done, errors in the absorption coefficient of 10 percent or more may occur.

To characterize the experimental accuracy, we suggest that $\alpha(\nu)/\rho_A^2$ is known to about ±5 percent. The relative accuracy is much better of course as may be seen from the small scatter of the experimental points.

4. THEORETICAL ANALYSIS

To analyze the data obtained here and previously,[1] particularly where there are partially resolved lines and bands, requires a line shape theory for collision-induced spectra. Such a theory has been recently developed and is presented in the report appended to this paper. As a test of the theory, it was found to represent accurately the translational band and S(0) line of eH_2 at 77K, and for the first time explain the blue shift of 17 cm^{-1} in the peak frequency of the S(0) line. The theory also represented well the translational spectrum of He-Ar and the rotational translational band of N_2 at room temperature. With such a theory, we are in a position to undertake a complete analysis of the far infrared spectrum of the H_2 and H_2-He mixtures as a function of temperature and ortho-para concentration, and obtain the induced dipole overlap parameters in collision between two para molecules and between an ortho and para molecule.

5. CONCLUDING REMARKS

Accurate data on the equilibrium collision induced spectrum of H_2 and H_2-He mixtures as a result of the work reported here and previously[1] are now available at 293, 195, and 77K from about 10 to 800 or 900 cm^{-1}. This wavelength region includes the translational band and the S(0), S(1), and S(2) rotational lines. The translational spectrum of normal H_2 has also been determined at 77K. With this and the translational spectrum for e-H_2, it may be possible to investigate differences in the interaction between isotropic and anisotropic H_2 molecules which are chemically identical.

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Figure 1. $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for H_2 at 293K.

Figure 2 $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for eH_2 at 195K. A dashed curve is used to represent the data in the frequency region where the data points are sparse.

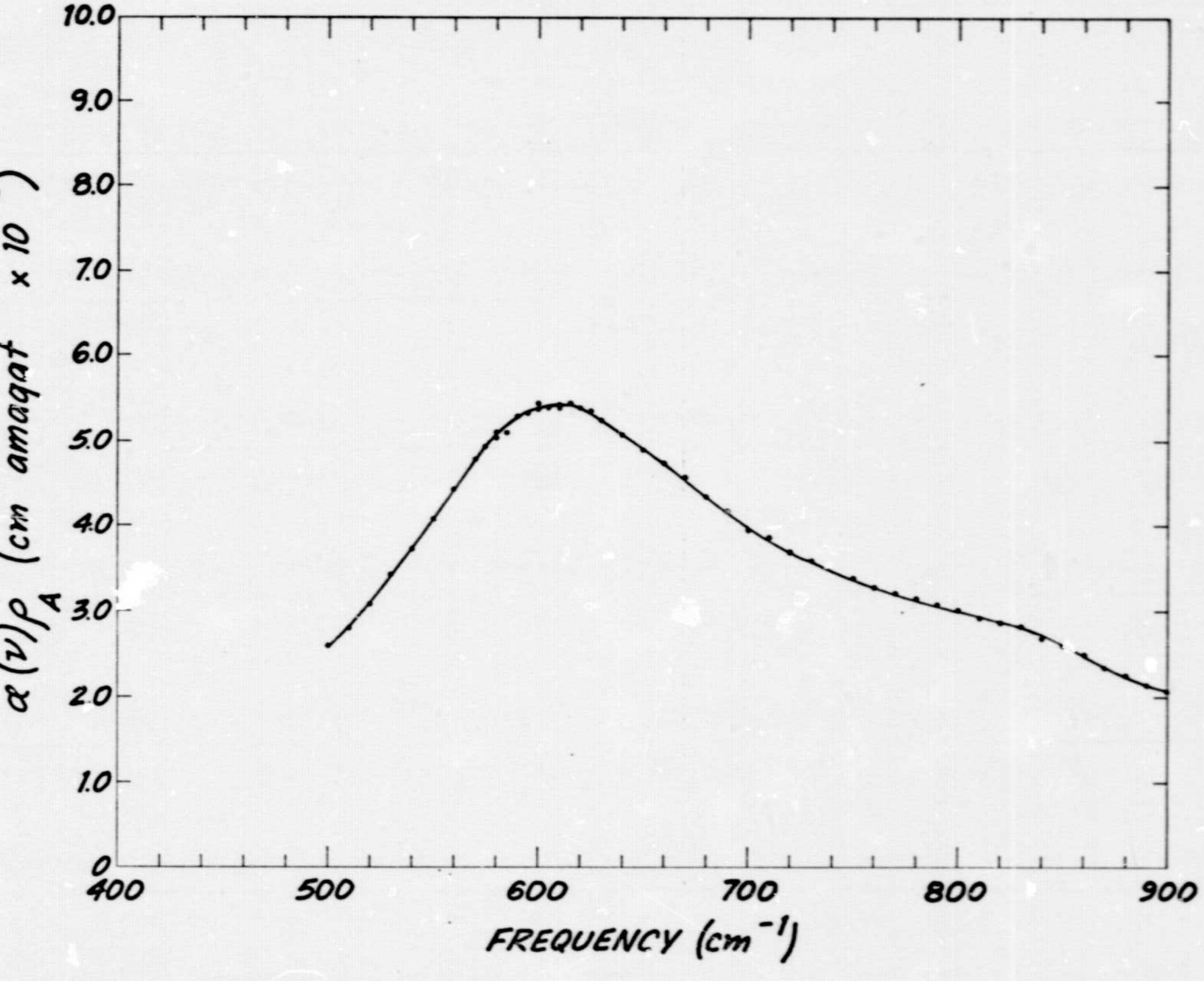
Figure 3. $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for eH_2 at 77.4K.

Figure 4. $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for a mixture of H_2-He containing 35.2 mole percent of H_2 at 293K.

Figure 5. $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for a mixture of eH_2-He containing 31.7 mole percent of H_2 (solid curve), and a mixture of H_2-He containing 35.2 mole percent of H_2 (dashed curve) at 195K. The dashed portion of the 31.7 mole percent H_2 curve between 465 to 500 cm^{-1} represents a region of sparse data points.

Figure 6. $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for a mixture of eH_2-He containing 31.7 mole percent of H_2 at 77.4K.

Figure 7. $\alpha(\nu)/\rho_A^2$ (cm^{-1} amagat^{-2}) versus ν(cm^{-1}) for nH_2 at 77.4K. The scale on the right applies to the complete spectrum. The low frequency portion of the spectrum is redrawn to the scale on the left.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8.0
7.0
6.0
5.0
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2.0
1.0
0
400
500
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700
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900
FREQUENCY (cm^{-1})

Figure 1

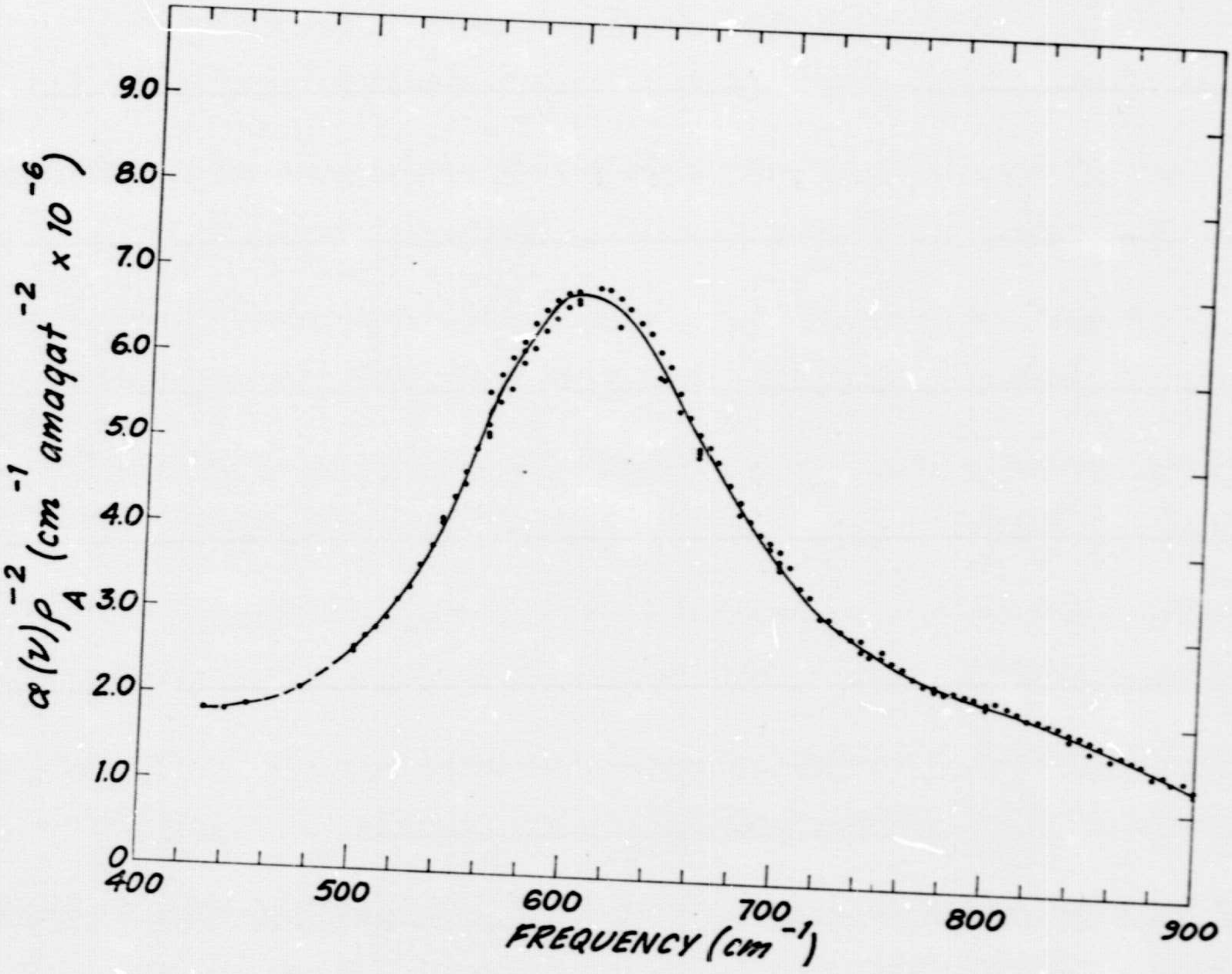

Figure 2

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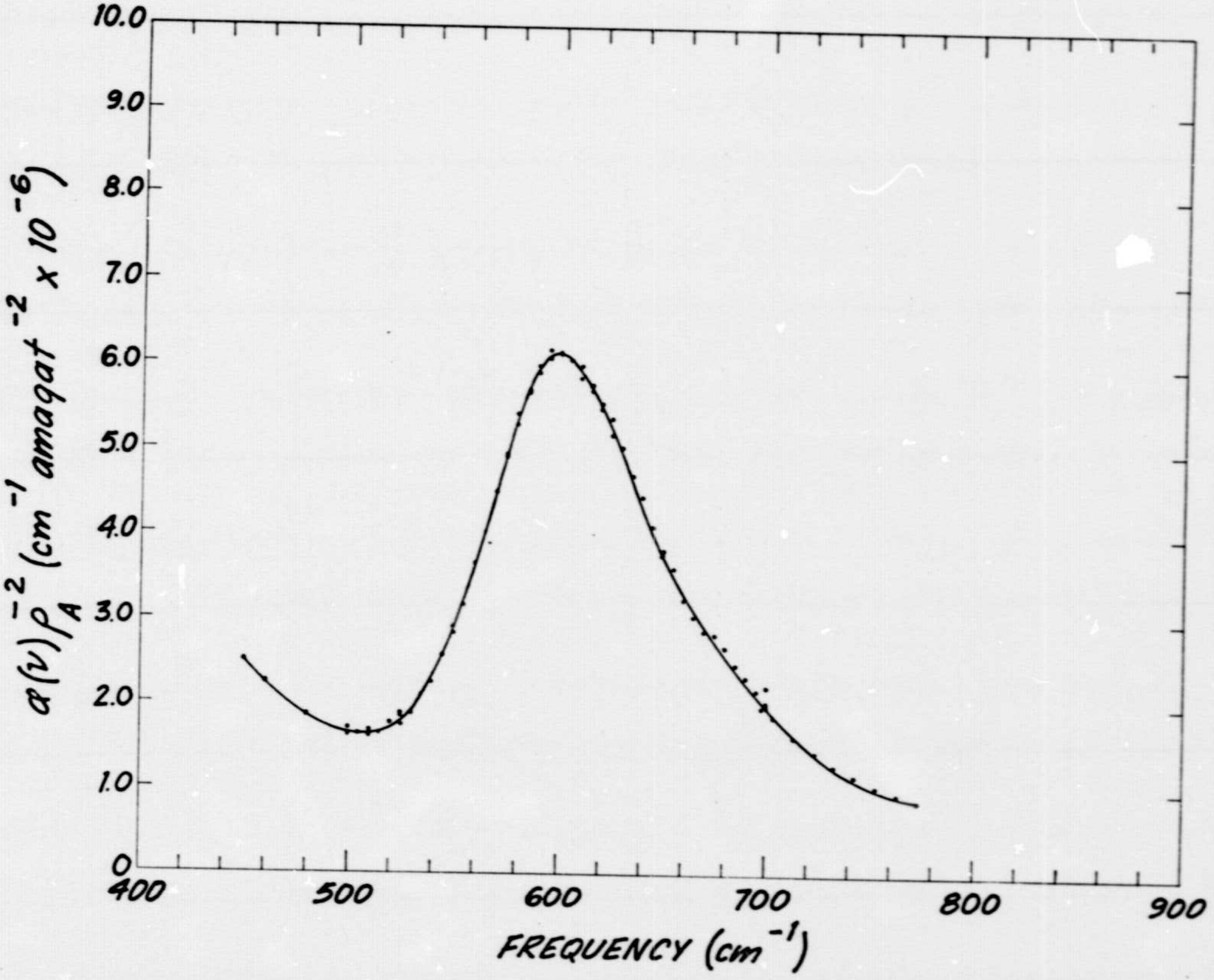
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9.0
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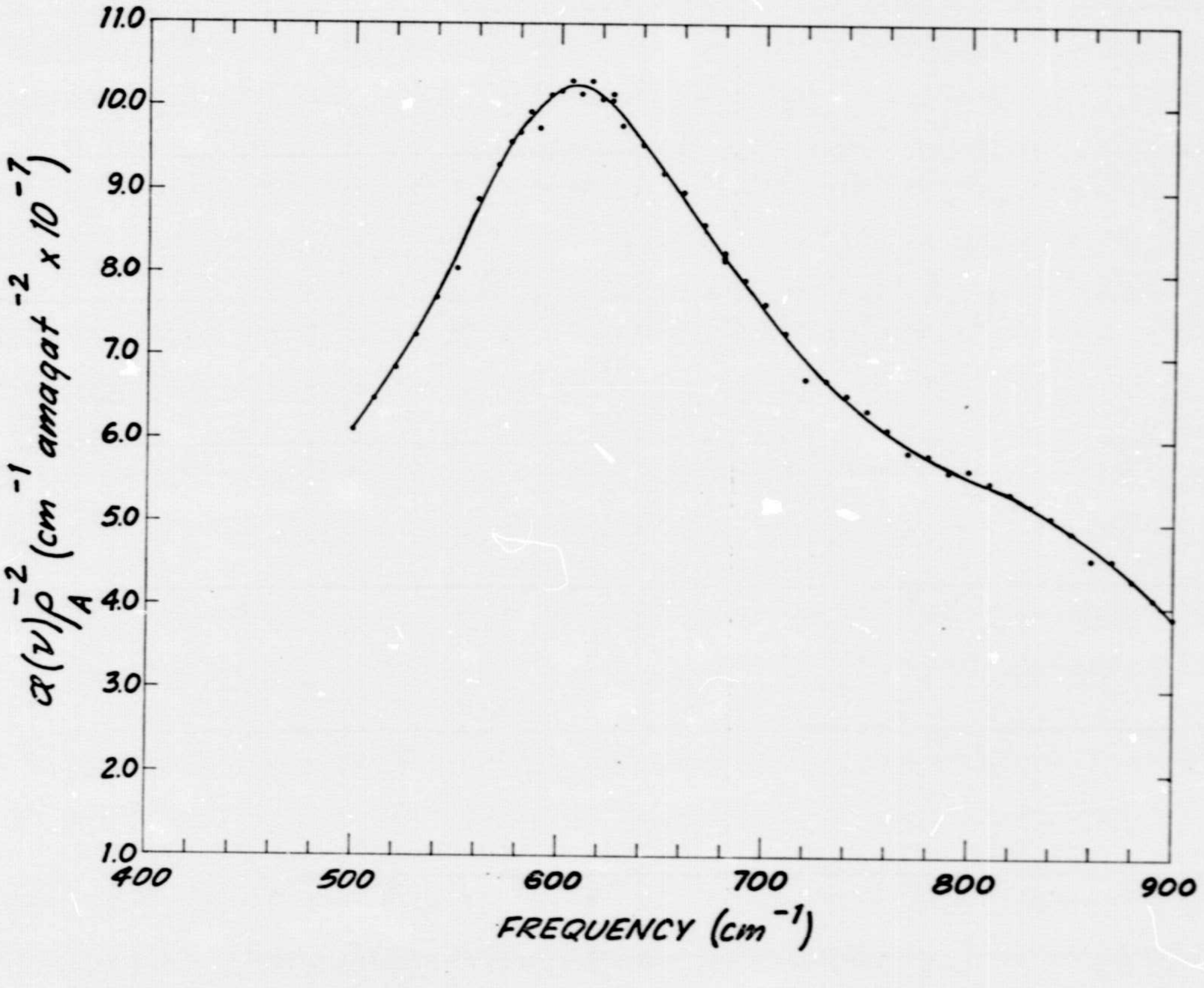
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
$\alpha(\nu)\rho_A^{-2}$ (cm^{-1} amagat^{-2} x 10^{-6})
400
500
600
700
800
900
FREQUENCY (cm^{-1})

Figure 3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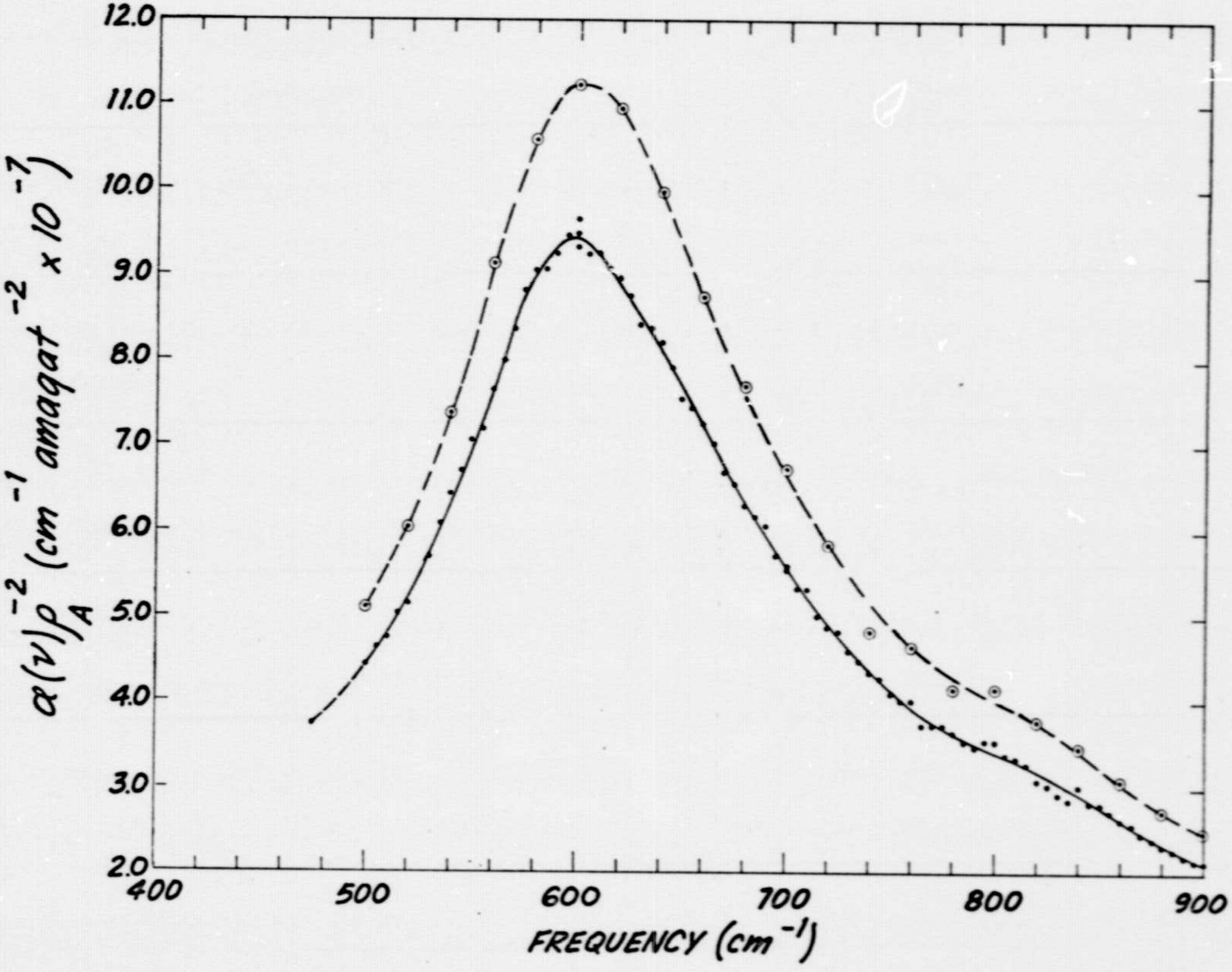
FREQUENCY (cm^{-1})

Figure 4



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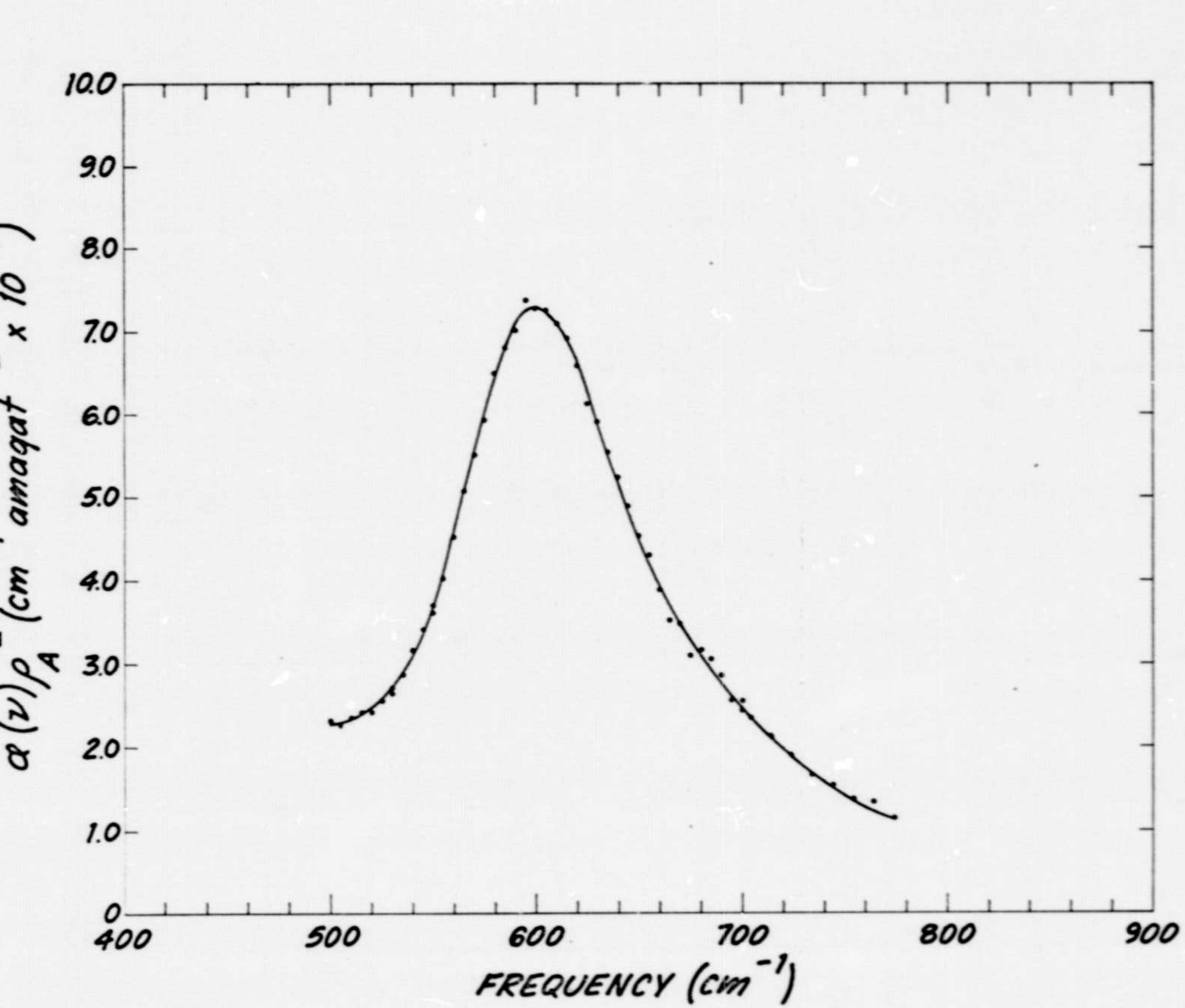
FREQUENCY (cm^{-1})

Figure 5


$\alpha(\nu)\rho_A^{-2}$ (cm^{-1} amagat^{-2} × 10^{-7})
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8.0
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6.0
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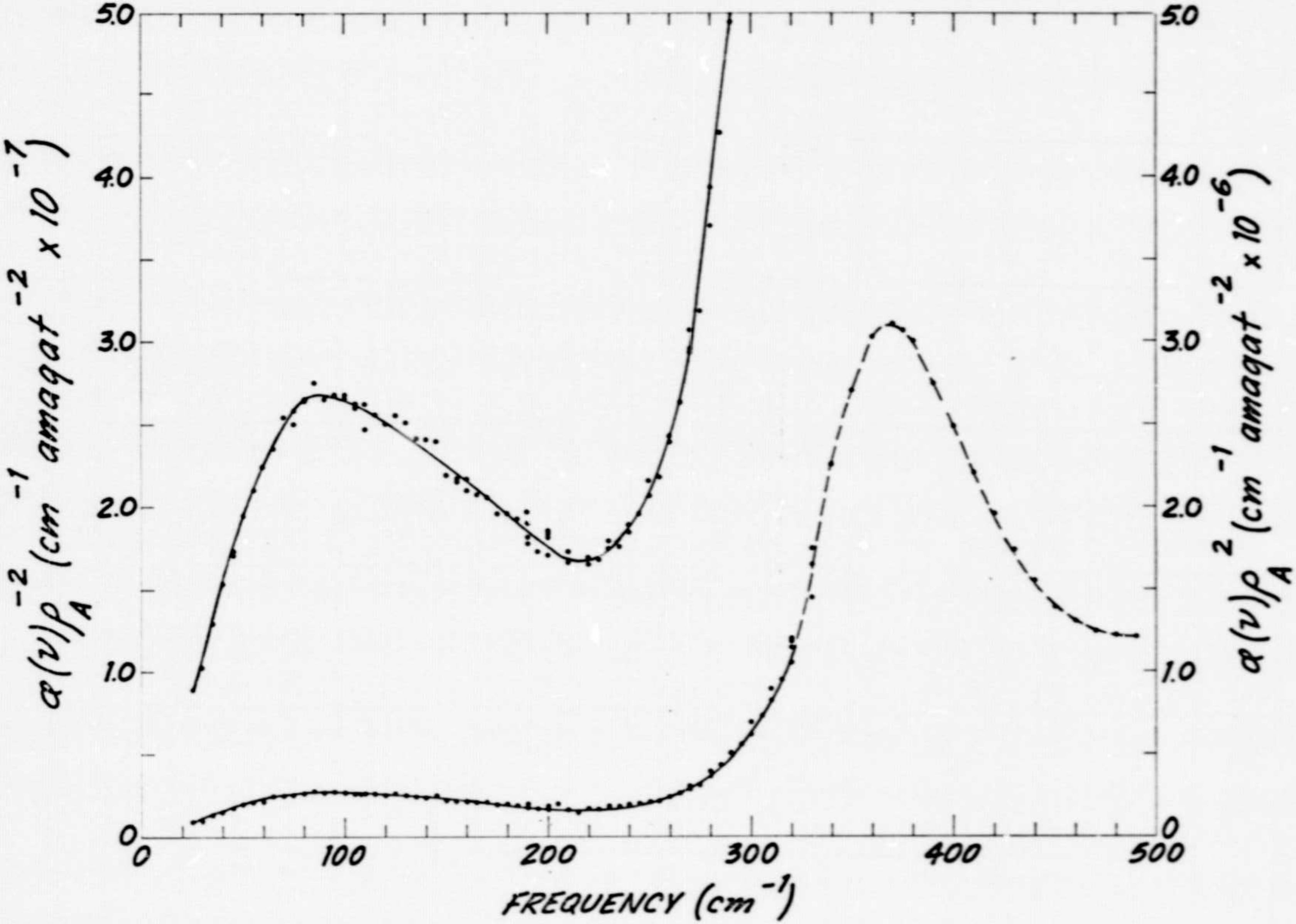
FREQUENCY (cm^{-1})

Figure 6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3.0
2.0
1.0
0
$\alpha(\nu)\rho_A^{-2}$ (cm^{-1} amagat^{-2} x 10^{-7})
$\alpha(\nu)/\rho_A^{2}$ (cm^{-1} amagat^{-2} x 10^{-6})
0
100
200
300
400
500
FREQUENCY (cm^{-1})

Figure 7