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THE EFFECT OF TEMPERATURE ON THE ABSORPTION BANDS OF FUSED QUARTZ IN THE INFRA-RED

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Abstract

The absorption bands of specimens of fused quartz, ranging in thickness from 2.0 mm for the 3μ region, to 4×10^{-4} mm for the 8μ region, were studied. In regions where sufficient energy was available, an echelette grating was used to give greater dispersion. Measurements were taken at room temperature and at 850°C. In accord with previous work, the absorption band in the region of anomalous dispersion at 9μ was found to shift toward longer wave-lengths with increasing temperature. With higher resolution, however, fine structure bands were found which did not shift with the temperature, but did undergo marked changes in intensity. Several sharp bands between 2 and 4μ were found to remain fixed as the temperature was changed. A broad band which proved to be double, was found at 12.5μ. These bands did not shift with temperature. In most cases, there was a marked change in intensity with temperature. It was found that inside the strong bands, the absorption was much less at high temperatures, while outside the bands, the reverse was the case.

Introduction

CONSIDERABLE work, extending over a period of more than a hundred years, has been done on the absorption of various substances. The study of temperature effects on the absorption bands has been almost equally extensive. The first observations of this kind were made by Brewster, who described a series of experiments in his Treatise on Optics, published in 1831. In these experiments, Brewster studied the effect on the transmission of various specimens of colored glass. These experiments at first appeared to give conflicting results, that is, in some cases an increase in the temperature caused an increase in the transmission, while in other cases, an increase in temperature made the glass opaque. In particular, Brewster found that blue glass when heated, transmitted first the yellow and finally the red, and as the glass cooled again, gradually cut off the red and yellow, transmitting only the blue. He found further that ruby glass when heated became practically opaque. Upon cooling, it again allowed the red to be transmitted.

These results, conflicting at the time, were later explained by the fact that the color of the glass was due to rather broad absorption bands which cut off one or more regions of the spectrum, and that these bands, or regions of absorption, shifted toward longer wave-lengths as the temperature was raised. Thus, if a broad band extends from the ultra-violet up through the yellow, heating the substance would cause the band to shift toward longer wave-lengths, finally cutting off all visible light. On the other hand, if there were no band in the near ultra-violet, but there was a band extending from the red end of the spectrum down through the yellow, then an increase in temperature would shift the band toward the red and finally out into the infra-red, thereby increasing the transmission. This shifting of the absorption bands toward longer wave-lengths with increasing temperature, was definitely shown by Conroy in 1891. He was the first to study the absorption bands with a prism spectrometer.

Temperature also has a marked effect on the intensity of the absorption bands, and a corresponding effect on the width of the bands. As early as 1852, Schonbein observed that substances that were highly colored at room temperature, became nearly white at very low temperatures. For example, sulphur appears white at −50°C. Many other substances behave in the same manner. An explanation of this loss of color at low temperature was made by Becquerel in 1907, while studying the effect of temperature on the absorption bands of the rare earths. Becquerel found that with decreasing temperature, the bands shifted slightly toward shorter wave-lengths. This was in accord with the work of previous investigators. He also found that at low temperatures, the absorption bands became very narrow, in some cases the bands were less than one-tenth as wide as at room temperatures. The bands were also found to be correspondingly more intense at the low temperatures.

In recent years, considerable work has been done on the absorption bands in the infra-red. H. Rubens and G. Hertz[1] studied the effect of temperature on the reflection maxima of calcite and crystal quartz in the infra-red. They made measurements of room temperature and at the temperature of liquid air. In the case of calcite, they found no shift in the reflection maximum as the temperature was changed. In the case of quartz, however, they claimed a slight shift of the maxima toward shorter wave-lengths as the temperature was lowered. From the observed points shown on the curves that were published, the only result that can be observed is a slight change in the relative intensity of the two bands. The position of maximum intensity remained fixed. This is in accord with results published recently by A. H. Pfund[2] who made a study of the reflection maxima of various substances in the region of anomalous dispersion. Pfund found that the reflection maximum of calcite at 6.5μ showed slight if any shift when heated to 510°C. In the case of amorphous substances, Pfund observed that the reflection maxima of fused quartz and glass in the region of 9μ underwent a marked shift toward longer wave-lengths as the temperature was increased, the shift for fused quartz being approximately 0.4μ when the temperature was changed from 40°C to 1100°C. The reflection maxima for glass were found to shift approximately 0.2μ when the temperature was raised from 40°C to 450°C. Pfund also found that with all substances studied, there was a progressive decrease in the reflecting power with increasing temperature. It was thought of interest to study the absorption in this region, so, at his suggestion, the following work under greater dis-

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[1] H. Rubens and G. Hertz, Berl. Ber. 256–274 (1912).

[2] A. H. Pfund, J.O.S.A. and R.S.I. **15**, 69–73 (1927).

persion, on the effect of temperature on the absorption of fused quartz in the regions from 2 to 12μ, was undertaken.

APPARATUS

The arrangement of the apparatus is shown in Figure 1. A Nernst glower, *N*, was used as the source of infra-red radiation. It was mounted in a small metal box to protect it from air drafts. It was operated from a storage battery. Since no other instruments were connected to the storage battery, the glower would reach a steady state after about fifteen minutes, and would then remain steady for several hours. It was found, however, that when a new Nernst glower was mounted, it was necessary to operate it for about an hour before it would reach a steady state. It was also noted that shortly before a filament burned out it became unsteady. The radiation from the Nernst glower was focused by the mirror, M_1, on the specimen of quartz, *Q*, to be studied. This specimen of quartz was mounted in a steel frame which fitted tightly in the furnace, *F*. The furnace consisted of a clay tube, 4 cm in diameter, and 15 cm long, around which were wrapped several turns of Nichrome wire. The heating element was protected by a thick layer of asbestos. The ends of the furnace were still further protected by asbestos hoods to prevent convection currents as much as possible. The furnace had a rather large heat capacity, and was well insulated, requiring about 45 minutes to reach a steady state. The temperature of the furnace was measured by means of a thermocouple and galvanometer. After passing through the specimen of quartz, the radiation was focused by the mirror M_2 on the first slit S_1 of the grating spectrometer. The radiation is then made parallel by the mirror M_3 and directed on the echelette grating[3] *G*.

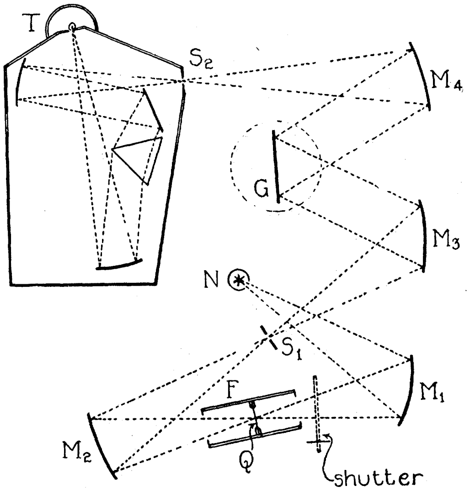

Fig. 1. Arrangement of apparatus.

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[3] Kindly loaned for this work by Dr. Wood.

The setting of the grating was made by observing the position of the image of a lamp filament reflected from a small mirror mounted on the axis of the grating. From the grating, the radiation was focused by mirror M_4 on the second slit of the grating spectrometer S_2. In order to prevent the overlapping of the various orders in the grating spectrum, a rock-salt spectrometer[4] was used. This consisted of a 60° rock-salt prism and mirror having a focal length of 30 cm, mounted according to Wadsworth. The second slit of the grating spectrometer was used for the first slit of the rock-salt spectrometer. Behind the second slit of the rock-salt spectrometer, was placed a compensating vacuum thermopile,[5] which in turn was connected to a D'Arsonval galvanometer having a period of about 5 seconds. To read the galvanometer deflections, a scale was mounted at a distance of 5 meters. The order of the grating and prism spectrometers in the present investigation, is the reverse of that used by W. W. Sleator[6] at the University of Michigan. Sleator used a prism of small angle and some difficulty was had in preventing overlapping in the near infra-red. In the present work, a regular 60° prism was used, and any overlapping of orders was entirely eliminated. The only reason for changing the order of the two spectrometers was the fact that the rock-salt spectrometer with thermopile already in place, was kindly placed at my disposal by Dr. Pfund. The grating spectrometer and the

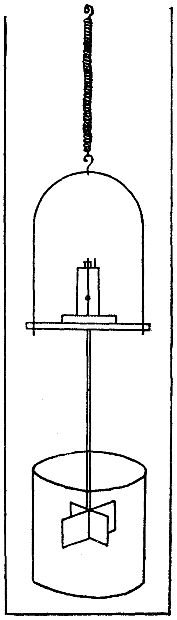

Fig. 2. Spring support for galvanometer.

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[4] Used by A. H. Pfund, J.O.S.A. & R.S.I. **15,** 69–73 (1927).

[5] A. H. Pfund, Phys. Zeits. **13,** 870 (1912).

[6] W. W. Sleator, Astrophys. J. **48,** 125 (1918).

rest of the apparatus were then constructed around it. The sensitivity of the vacuum thermopile was such that a candle at a meter's distance gave a deflection of 2000 mm.

One of the first difficulties to be overcome was the unsteadiness of the galvanometer deflection due to vibration of the building. Mounting the galvanometer on a wall bracket and resting the galvanometer on a thick felt pad cut down the vibration to some extent, but it was necessary to take readings between 12 and 4 o'clock in the morning. Finally, a spring suspension was used. The arrangement is clearly shown in Figure 2. The suspension consisted of a heavy platform supported by a long spring having a very slow period. A long rod having crossed vanes on its lower end, was rigidly attached to the base of the platform. The vanes were immersed in heavy oil to damp out any oscillation set up by air drafts. To prevent air drafts as much as possible, shields were built around the galvanometer and suspension. This arrangement was very steady, in fact, striking the wall near the galvanometer support a sharp blow with a hammer caused no change in the galvanometer deflection, and a deflection of 0.01 mm could have been detected. With the arrangement thus described, it was possible to take readings to less than 0.1 mm at a scale distance of 5 meters. To obtain these readings, a very narrow diffraction band from a lamp filament was focused on the scale of a micrometer eye-piece. The width of the image thus formed was about 0.05 mm.

RESULTS

Considerable difficulty was encountered in obtaining films of quartz thin enough to be sufficiently transparent in the region of 9μ. Films having a thickness of 0.01 mm were absolutely opaque in this region. By using a very hot oxygen torch, it was possible to blow some thin quartz bulbs having a thickness of 1.5×10^{-3} mm. The thickness of the various specimens was determined by the channeled spectrum method.

With a film of quartz having a thickness of 1.5×10^{-3} mm, the curves shown in Figure 3 were obtained. The absorption was measured for temperatures of 25°, 780°, and 1100°C. As can be seen from the curves, the band is very broad and extremely deep, the transmission in the deepest part of the band being only 0.2 percent. As the temperature was increased, a progressive shift of the absorption region toward longer wave-lengths was observed. A marked increase in transmission was also observed at the higher temperatures, and a corresponding broadening of the band. The actual shift of the region of absorption was approximately 0.4μ.

A very interesting result appeared at about 9.45μ, namely a slight, transparent region which did not shift as the temperature was changed. This small transparent region was found in every set of observations, very decided in some cases, while in others it appeared as a sharp change in the inflection of the curves. This transparent region suggested the probability of a small band on either side which did not shift with temperature, but which did change their relative intensity with increasing temperature.

The problem was then to obtain very much thinner films of fused quartz. Several methods were tried without success. Some of the thinnest films were immersed in hydrofluoric acid. This was not satisfactory, for while it did make the films thinner, they were not of uniform thickness, and could not be used. The first method was again resorted to, and finally a bulb was blown thin enough to show Newton's colors. A small film from this was obtained having a thickness of only 4×10^{-4} mm, or about one-twentieth of the wave-length of light in the region to be studied. This specimen was many times more transparent, and gave much better results as shown in Figure 4. Unfortunately this film was not quite large enough to take advantage of all the energy available but this was more than made up by its greater transparency. In this case measurements were made at 25° and 850°C. A marked increase in transmission at the higher temperatures was observed, as in the previous case. Distinct bands were found at 9.28, 9.40, and 9.55μ. A sharp bend in the curve for high temperature was observed at about 9.34μ which was not so pronounced at low temperature. The position of the maximum for all these bands remained fixed as the temperature was varied, which shows definitely that, while the region as a whole shifts toward longer wave-lengths with increasing temperature, the fine structure bands within the region remain fixed. Attention is called to the marked reversal of the relative intensity of the 9.40 and 9.55 μ bands. This change in the relative intensity of the fine structure bands with temperature is probably the cause of the apparent shift of the region as a whole. In all cases, two observations

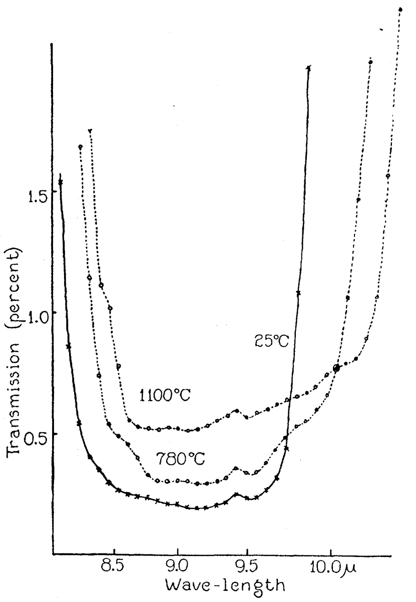

Fig. 3. Transmission of quartz film 1.5×10^{-3} mm thick.

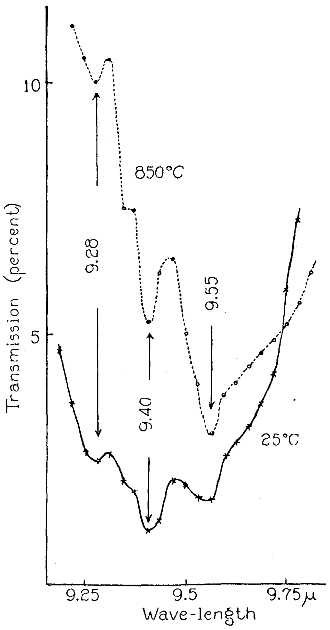

Fig. 4. Transmission of quartz film 4×10^{-4} mm thick.

were made with the specimen at room temperature, one before the high temperature readings were taken, and one afterwards. No permanent change in the absorption as a result of heating was observed, the two sets of data checking well within the range of experimental error.

A detailed study was next made of the absorption of fused quartz between 2 and 4μ. For this purpose, an echelette grating, having 2000 lines per inch and concentrating in the region of 3.5μ, was used. The effect of temperature on the absorption bands in this region is shown by the curves in Figure 5. The band at 2.71μ was very sharp, being slightly less intense at the high temperature and correspondingly broader. The position of the maximum remained fixed as the temperature was changed from 25°C to to 850°C. As before, low temperature readings were taken before and after the high temperature readings, and no permanent effect of the heating was observed. Small bands at 3.83μ and 3.90μ did not shift with temperature, but there was a marked increase in absorption of the whole region with increasing temperature. The relative intensity of these two bands remained practically the same as the temperature was changed. A rather weak band was observed at 3.54μ, slightly more pronounced at the higher temperature. A sharp bend in the curves occurred at 3.35μ, and although there was a marked increase in the absorption at this point, the position of the bend was not changed as the temperature was raised. Small bands were found at 2.40μ and 2.51μ, the intensity of the bands being slightly greater at the high temperature, but remaining fixed in position. Two small bands were found at 2.93μ and 3.00μ. These bands were always present in the several sets of observations made, but there was a marked change in intensity of these bands in different observations, even at the same temperature. T. Dreish[7] has made a study of the absorption of fused quartz and crystal quartz in the 3μ region. He found bands for crystal quartz at 2.91μ and

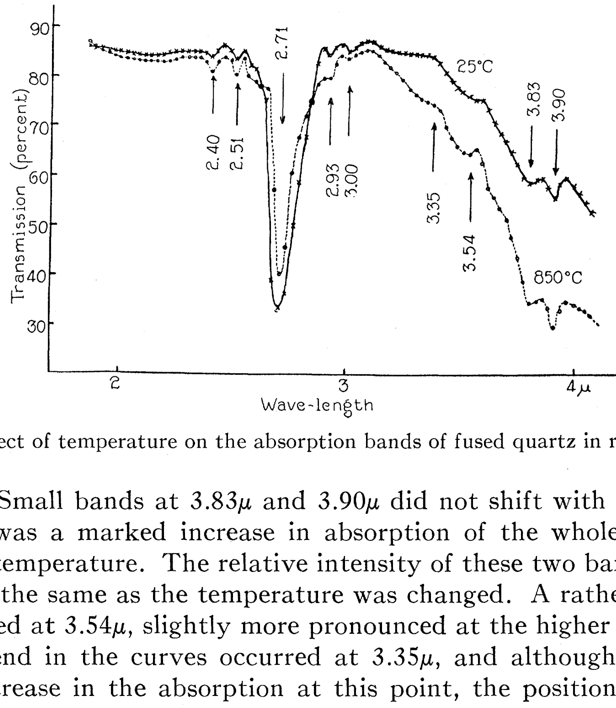

Fig. 5. Effect of temperature on the absorption bands of fused quartz in region of 3.5μ.

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[7] T. Dreish, Zeits. f. Physik **42,** 426–427 (1927).

3.02μ which correspond almost exactly to those mentioned in the present work at 2.93μ and 3.00μ. From this fact, and since fused quartz is a super-

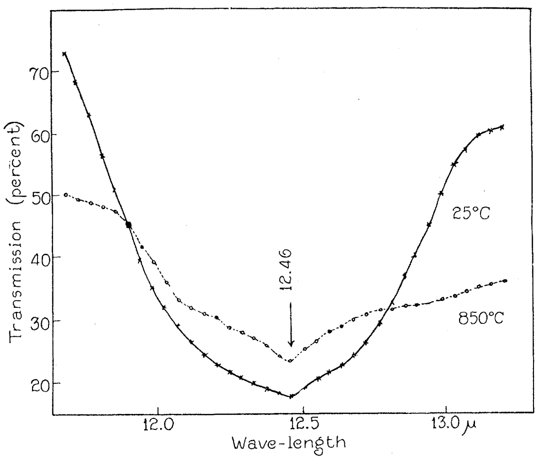

Fig. 6. Effect of temperature on the absorption bands of fused quartz in region of 12.5μ. Thickness of quartz 3×10^{-3} mm.

cooled form that reverts very slowly at low temperatures to the natural form, namely, crystal quartz, it was thought that there might be slight traces of crystalline structure present, which might be the explanation of these bands. The specimen was examined under a strong microscope with

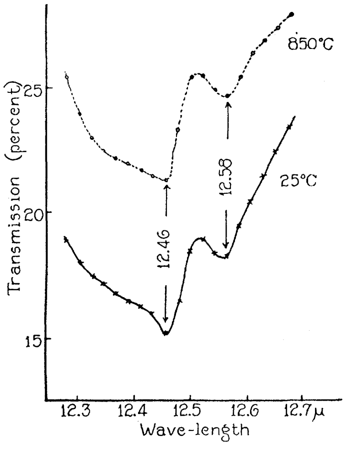

Fig. 7. Effect of temperature on the absorption bands of fused quartz in region of 12.5μ. Thickness of quartz 2×10^{-3} mm.

polarized light, and it was found to have a very slight structure. While these bands may thus be due to crystal quartz, it is possible that these bands occur in both forms but with very great differences in the relative intensity in the amorphous and crystal form. E. K. Plyler[8] found a very slight band in crystal quartz which corresponds to the very intense band in fused quartz at 2.71μ.

A study was next made of the absorption of fused quartz in the region of 12μ. With a film of quartz of thickness 3×10^{-3} mm, the curves of Figure 6 were obtained. The absorption region is very broad, showing a maximum at 12.46μ. A thinner specimen, 2×10^{-3} mm, was then used. The band was clearly shown to be double as seen in Figure 7. Besides the band at 12.46, there was a band of less intensity at 12.58μ. The intensity of the absorption region was much less at the high temperature, 850°C. The relative intensity of the two bands did not change with the temperature, and the position of the maxima remained fixed, as in all the previous cases. A marked broadening of the band was observed at the high temperature.

Thus it appears that the individual fine structure bands do not change their position with temperature, although there is in some cases a relative change in the intensity of two neighboring bands which results in an apparent shift toward longer wave-lengths with increasing temperature for the unresolved band. In general, the bands are broader and correspondingly less intense at the higher temperature.

Discussion

As to the nature of these bands, it is evident that they must be due to vibrations within the molecule itself. It has been suggested by E. K. Plyler,[8] that the bands at 9μ, 12.5μ, 21μ, and 26μ are fundamental bands. This assumption is made on the basis of the great intensity of the bands, and on their position in the spectrum. In view of the results of the present work, however, it is possible that the fine structure bands at 9μ are, themselves, combination bands rather than fundamental bands. In the first place, temperature should not affect greatly the relative intensity of the fundamental bands. A fundamental band corresponds to an energy change of $\delta n=1$. This amount of energy is absorbed in a jump from the level $0\rightarrow 1$, $1\rightarrow 2$, or $2\rightarrow 3$, etc. If the vibration were truly harmonic, the energy change, corresponding to a jump between any two consecutive energy levels, would be the same. But since the vibration is not exactly elastic, the energy, and accordingly the frequency, will be different in each case. The deviation from the true harmonic oscillator is a function of the temperature. Hence, a change in temperature would be expected to cause a change in the wave-length of the various bands. This effect, however, is of the same order of magnitude as the expansion of the substance with temperature, and is, therefore, too small to be detected with the present infra-red methods.

On the other hand the combination bands result, primarily, from the deviations from the true harmonic oscillator, due to coupling between the vibrators, and since this deviation depends on the temperature, one would

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[8] E. K. Plyler, Phys. Rev. **33,** 48–51 (1929).

expect marked changes in the intensity of combination bands with temperature.

Referring again to Figure 4, it is observed that the intensity of the bands at room temperature is as much as 500 percent greater than at a temperature of 850°C. Furthermore, if the bands found by Pringsheim and Rosen[9] using the Raman method, at 38μ and 80μ, together with those previously found at 26μ and 2 =μ, and the two observed in the present work at 12.46μ and 12.58μ are used to calculate combination frequencies, the fine structure bands at 9μ appear as simple combinations of the bands of longer wave-length. If we denote the frequency corresponding to 12.46μ by ν_1, 12.58μ, by ν_2, 21μ by ν_3, 26μ by ν_4, 38μ by ν_5, and 80 by ν_6, the following results are obtained:

Combination	Wave-lengths	
	Calculated	Observed
$(2\nu_3+\nu_6)$	9.28μ	9.28μ
$(\nu_1+\nu_6)$	9.39μ	9.40μ
$(\nu_2+2\nu_6)$	9.57μ	9.55μ

Whether these bands at 9μ are combination bands or not, the fact still remains that the frequency of vibration is not appreciably altered by a large change in temperature, although the number of vibrators affected by coupling may vary in a marked manner as the temperature is changed, which results, in some cases, in the great variation in relative intensity of the combination bands with temperature.

An attempt to check the bands found in the region between 2μ and 4μ by the combination principle was made with the following results:

TABLE I. *Interpretation of bands between 2μ and 4μ as combinations.*

Combination	Wave-lengths		Combination	Wave-lengths	
	Calculated	Observed		Calculated	Observed
$(5\nu_1+\nu_6)$	2.42μ	2.40μ	$(4\nu_1+\nu_6)$	3.01μ	3.00μ
$(3\nu_1+2\nu_2)$	2.51μ	2.51μ	$(3\nu_3+4\nu_4)$	3.36μ	3.35μ
$(3\nu_1+3\nu_3)$	2.63μ	2.62μ	$(3\nu_3+3\nu_4+2\nu_6)$	3.52μ	3.54μ
$(4\nu_2+2\nu_5)$	2.71μ	2.71μ	$(3\nu_2+2\nu_6)$	3.80μ	3.83μ
$(4\nu_2+\nu_5)$	2.91μ	2.93μ	$(2\nu_1+2\nu_3)$	3.92μ	3.90μ

The damping, which results from the deviation from the simple harmonic oscillator, produces the well-known effect of broadening the absorption band. And as this damping is a direct function of the temperature, the broadening would be expected to increase with increasing temperature. This was found to be the case. The increased broadening of a band was always accompanied by a corresponding decrease in the intensity of the band. This was to be expected from the fact that the amount of energy absorbed in the whole band depends directly on the number of absorbing vibrators that are present, and, since this number is constant for fundamental bands (except for the small change due to expansion of the material), the amount

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[9] Pringsheim and Rosen, Zeits. f. Physik **50**, 741–755 (1928).

of energy absorbed must be constant. Hence, when the band becomes broader, it must necessarily become correspondingly less intense.

While it is true that the frequency is not changed with temperature when the material has undergone no change of form, other than the slight thermal expansion, it is quite probable that where there are changes in the form of the substance with temperature, there will be a corresponding shift of the absorption bands. It is the intention to study this problem in the near future.

In conclusion, I wish to express may appreciation to Dr. Pfund, who suggested the present investigation and was a continuous source of help and inspiration throughout the progress of the work, and to Dr. Wood for the loan of gratings and for helpful suggestions from time to time. I also wish to thank Dr. Herzfeld for his help in discussing the results and his kindly interest in the work in general.