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Abstract

Measurements of the absorption of 5-mm radiation in oxygen gas have been made. The experimentally observed magnitude and shape of the absorption may be satisfactorily compared with the theoretical curves of Van Vleck for an assumed line breadth $\Delta\nu \cong 0.015$ to 0.02 cm^{-1} . Observations of the absorption in mixtures of oxygen and nitrogen indicate a disparity of O_2 and N_2 collision cross sections. It is suggested that nitrogen causes an anomalous narrowing of the oxygen absorption line breadth.

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Introduction

The existence of an absorption band in the millimeter region due to molecular oxygen has been predicted and discussed at some length by Van Vleck(1). Measurements made by Beringer(2) have given a preliminary confirmation of the existence of this absorption band, as have those of Lamont(3). A more detailed investigation of the absorption of 5-mm radiation by oxygen will be reported here.

As Van Vleck has pointed out, the oxygen molecule is in a $^3\Sigma$ ground state, since it has one unit of spin angular momentum. As a consequence of this resultant spin, it has a magnetic moment equal to two Bohr magnetons. This permanent magnetic moment is the cause of the paramagnetism observed in oxygen, and it also allows the molecule to couple to the magnetic field of an electromagnetic wave. The unit of spin angular momentum perturbs the rotational state since it is coupled to the rotational motion of the molecule. The unit electron spin has three spatial orientations with respect to the given molecular rotational angular momentum vector, K , so that each rotational level is split into three states, $J = K + 1$, K , and $K - 1$, each J state of this so-called ρ -type triplet arising from a different orientation of the spin with respect to the rotational motion of the molecule. The energy difference between successive J terms in any of these triplets is about 2 cm^{-1} (with the single exception of $J = 0 \rightarrow 1$ difference which is about 4 cm^{-1}). Selection rules for magnetic dipole transitions allow induced transitions between these successive members of the triplet ($\Delta J = \pm 1$) so that for each value of the rotational angular momentum quantum number K there are two absorption frequencies in the 2 cm^{-1} region. The population of the various rotational levels follows Boltzmann statistics, and it may be shown that the most populated state at room temperatures is that one for which $K = 13$. States with $K \cong 25$ still have significant populations however. The ^{16}O nucleus has zero nuclear spin angular momentum, so that symmetry considerations demand that K have only odd values. Thus, with two absorption lines for each value of K , there are about 25 lines which overlap at atmospheric pressure and which contribute significantly to the absorption in the 2 cm^{-1} region. Van Vleck(1) has calculated the shape and magnitude of the absorption for various values of the line-broadening parameter $\Delta\nu$. The theory uses the values of the triplet spacings as determined from optical spectroscopy, and is totally determined except for line-broadening or line-breadth parameter $\Delta\nu$. The intensity is not sensitive to the assumed triplet spacings but it is a strong function of the line

breadth $\Delta\nu$. For this reason, previous measurements(2)(3) have obtained the magnitude of the absorption at a few scattered points and have inferred the line breadth $\Delta\nu$ from this intensity. The measurements below are an extension of previous measurements in that the theory is essentially checked by comparing both the intensity and structure of the measured and computed absorption.

Apparatus

A balanced microwave bridge was used to measure the absorption. Five-mm power was obtained from the second harmonic generated in a nonlinear silicon crystal driven by a 1-cm reflex klystron oscillator. A block diagram of the apparatus is shown in Figure 1. The 5-mm radiation was then divided between two nearly identical waveguides and recombined in a bridge T-junction. One output arm of the T fed a matched load and the other fed a harmonic converter. The converter mixed the incoming 5-mm radiation with the second harmonic of another 1-cm local oscillator, and the heterodyne signal current was fed to a 24-Mc/sec amplifier. Provisions were made for inserting a step-attenuator pad in the amplifier cascade after three stages of amplification.

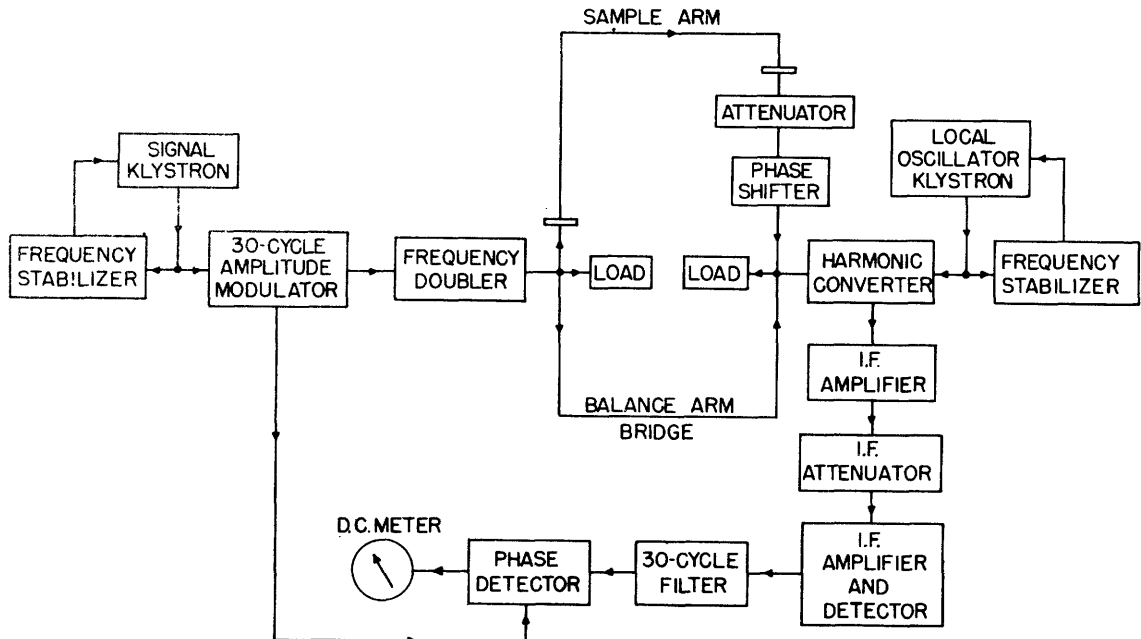


Fig. 1. Block diagram of absorption-measurement apparatus.

Both the signal oscillator and local oscillator were frequency-stabilized to a high mode of a 3-cm cavity using a Pound(4) and, later, a Zaffarano(5) circuit. The frequency of the signal-generator fundamental was measured with

the M.I.T. frequency standard(6). The signal-generator fundamental was amplitude-modulated with a rotating attenuator at 30 cycles/sec. The detected output from the receiver could then be filtered for the 30-cycle modulations. This modulation was amplified and converted to d-c with a phase detector. The signal was read on a milliammeter and the 30-cycle modulation merely provided a convenient monitoring current to amplify after filtering.

In operation, the sample arm of the bridge was filled with tank oxygen at 80 cm Hg, and the bridge balanced for no receiver output by means of the r-f phase shifter and attenuator in the sample arm. The sample was then pumped out and the bridge rebalanced as well as possible by slowly admitting tank argon into the sample arm to an appropriate pressure. The final minimum was achieved with readjustment of the r-f phase shifter. The use of argon for rebalancing allowed the bridge to work under constant impedance conditions. This procedure proved necessary for accuracy. Argon was chosen because its dielectric constant is similar to that of oxygen. Since argon is monatomic, it has no absorption in the region of these measurements. Check measurements on nitrogen, using argon as a balancing agent, disclosed no absorption greater than 1 db/km. The minimum signal current was noted and the phase shifter was readjusted to give a maximum output; the 24-Mc/sec step attenuator was then introduced and the current-output reading was made as nearly equal to that observed at minimum balance as was possible. The attenuator had a minimum change of 1 db and the readings were taken to 0.5 db by interpolation. The attenuator reading then gave the value of the maximum-to-minimum power ratio as:

$$\text{db} = 10 \log (P_{\max}/P_{\min}) .$$

It can be shown that the attenuation in the gas may be calculated as:

$$\Delta P/P = 4\alpha^{1/2}/(1 + \alpha^{-1/2})^2 .$$

where

ΔP = power absorbed,

P = incident power on sample,

$\alpha = P_{\max}/P_{\min}$

The path length was 6.15 m and, when correction has been made for changing from a guided path to a free-space path, the attenuation γ in db/km is given as:

$$\gamma = -10(\lambda_0/l\lambda_g) \log (1 - \Delta P/P) \text{ db/km,}$$

where

λ_0 = free-space wavelength,

λ_g = guide wavelength,

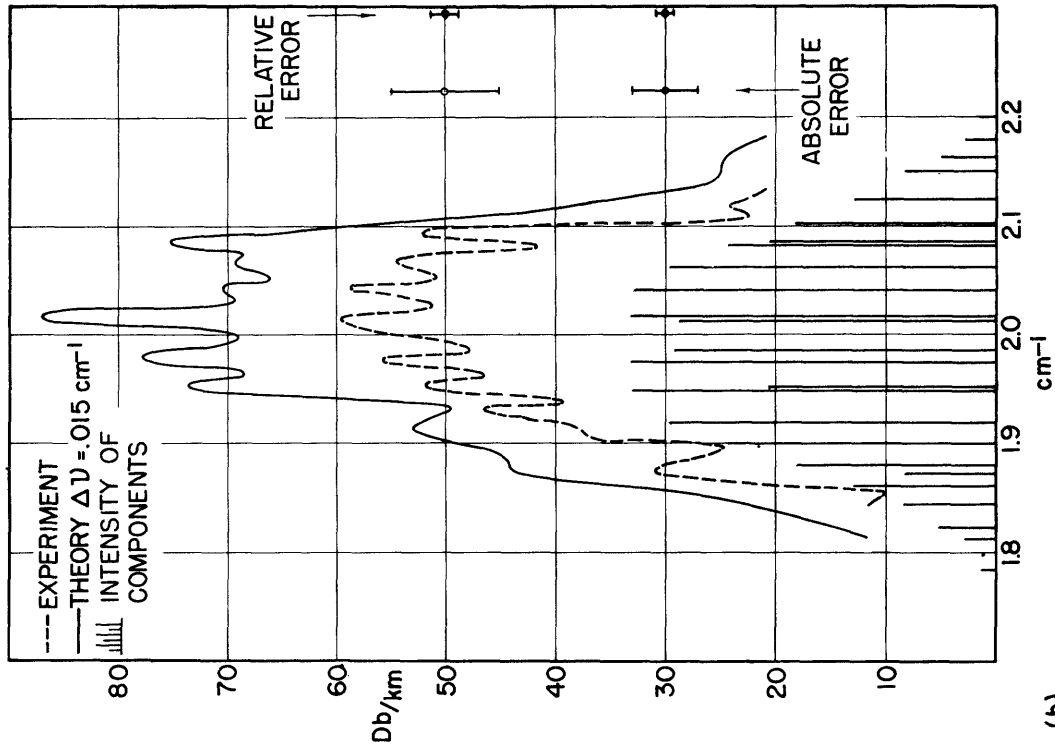
l = absorption path length in kilometers.

A stable balance with a P_{\max}/P_{\min} of 60 db could be readily obtained; this is the balance required to read to 2.5 db/km. The attenuator was correct to ± 1 db in magnitude, and relative readings were good to the setting accuracy of ± 0.5 db. Stated otherwise, the data are good to ± 10 per cent in absolute value and to less than ± 5 per cent in relative value. Several readings were made at each frequency, and the frequency intervals were about $.003 \text{ cm}^{-1}$. Readings at approximately 100 different frequency settings with oxygen at 80 cm Hg pressure were used to compile the final results. Readings were also made at some frequencies for oxygen-nitrogen mixtures.

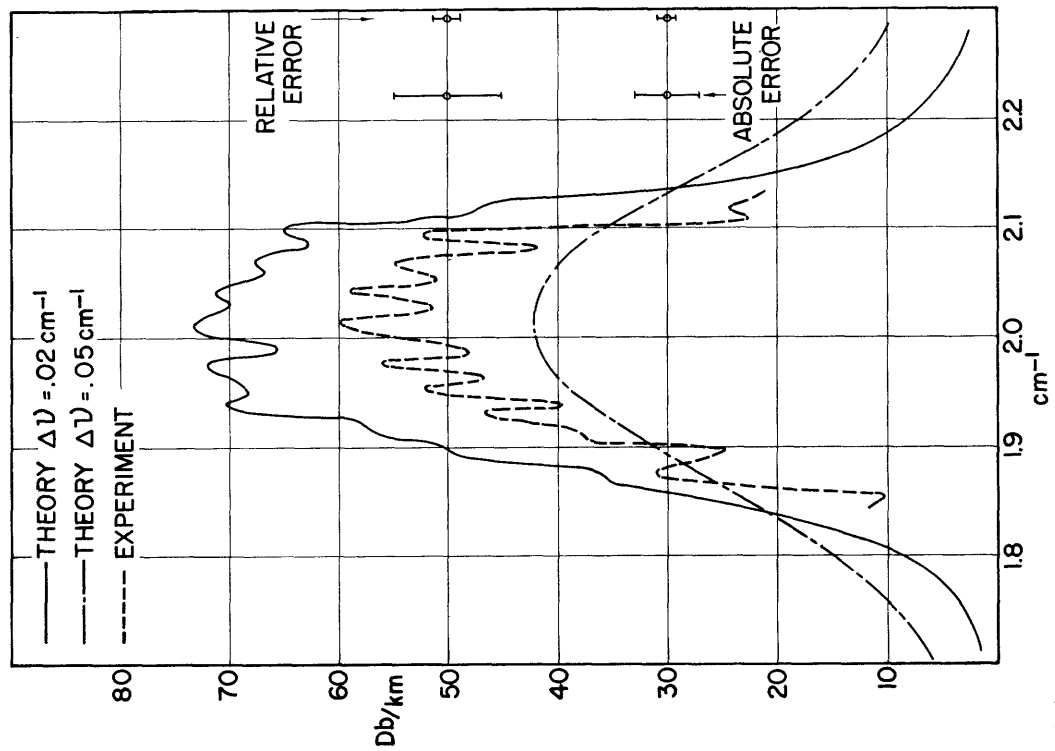
Absorption by Pure Oxygen

The data obtained for pure oxygen at 80 cm Hg pressure are shown plotted in Figure 2 (a), together with two curves of predicted absorption at 80 cm Hg pressure for line breadths $\Delta\nu = .02 \text{ cm}^{-1}$ and $.05 \text{ cm}^{-1}$. The curve for $\Delta\nu = .02 \text{ cm}^{-1}$ is derived from that of Lamont(3) which was computed using the new Babcock evaluation of the triplet energy difference. It is in slightly better agreement with the experimental data than the curve of Van Vleck for which the older values of Dieke and Babcock were used. The curve of absorption for $\Delta\nu = .05 \text{ cm}^{-1}$ at 80 cm Hg pressure is derived from that of Van Vleck (1).

A line breadth of $.05 \text{ cm}^{-1}$ is obviously too high. The curves match rather well for a line breadth of $.02 \text{ cm}^{-1}$, although the experimental absorption is about 20 per cent low. Figure 2 (b) shows the plotted experimental data, together with a computed curve for $\Delta\nu = .015 \text{ cm}^{-1}$. The structure of these two curves registers rather well. The magnitude of the measured absorption is low, in this case by about 35 per cent. The discrepancy in magnitude is not unreasonable. In a similar case, the observed absorption in H_2O at $.74 \text{ cm}^{-1}$ is 10 to 20 per cent below the theoretical value, depending upon the value of the electric dipole moment used (7)(8). So it may be said that, assuming a line breadth of $.015 \text{ cm}^{-1}$, there is a satisfactory agreement between theoretical and experimental values of the 2 cm^{-1} absorption in O_2 at 80 cm Hg and 293° K .



(a)



(b)

Fig. 2 Experimental data for absorption vs. frequency, in pure oxygen at 80 cm Hg, plotted with a computed curve for
 (a) $\Delta\nu = .05 \text{ cm}^{-1}$ and $.02 \text{ cm}^{-1}$
 (b) $\Delta\nu = .015 \text{ cm}^{-1}$.

It may be noted that the line breadth predicted from the collision cross section given by kinetic theory is about $.04 \text{ cm}^{-1}$. There is a certain amount of difficulty in justifying a line breadth smaller than that given by the mean free time. For simple microwave spectra, it has been generally found that the observed line breadths are greater than those predicted by the mean free time because of dipole-dipole perturbations. In the absence of large dipole interactions, line breadths narrower than those computed from kinetic theory are possible if all collisions are not effective in interrupting the absorption processes. Since the molecular translational energy follows a Boltzmann distribution, from energy considerations, some collisions are conceivably ineffective, hence a narrower line breadth. This point should undoubtedly be further investigated theoretically.

Oxygen-Nitrogen Mixture

Measurements were also made of the absorption in oxygen diluted with nitrogen. This was done to determine the scaling factor needed to reduce the measurements on pure oxygen to their air equivalent (21 per cent O_2 , 79 per cent N_2). We had expected to find a simple linear relationship between pure and dilute oxygen absorption. Since O_2 and N_2 collision cross sections should be nearly the same, the line breadth should remain essentially constant with a constant total pressure. The reduction in absorption would then vary proportionally to the number of absorbing oxygen molecules.

Absorption in oxygen-nitrogen mixtures was measured in the fashion described above for pure oxygen. The total pressure of the mixture was held constant at 80 cm Hg and the partial pressure of oxygen was varied between 5 and 80 cm Hg. The relationship between absorption and oxygen partial pressure proved to be complex. Several curves of absorption versus oxygen partial pressure taken at different frequencies are shown in Figure 3. The behavior of the absorption with varying oxygen content is difficult to justify with any simple picture of the absorption process.

In Van Vleck's notation, the data of Figure 3 were taken for the region between the $K_- = 9$, $K_+ = 3$ and the $K_- = 7$, $K_+ = 5$ transitions. Since the characteristic line breadth is the only factor undetermined in the Van Vleck-Weisskopf theory, there remains only the possibility of variation of this parameter with nitrogen dilution. If the line breadth were to increase with increasing dilution, the curves of Figure 3 would have the opposite curvature, i.e., a curvature away from the axis of partial pressure. If the line breadth were to decrease with increasing oxygen dilution (a situation which might be accounted for by a decrease in dipole-dipole interaction), the curvature

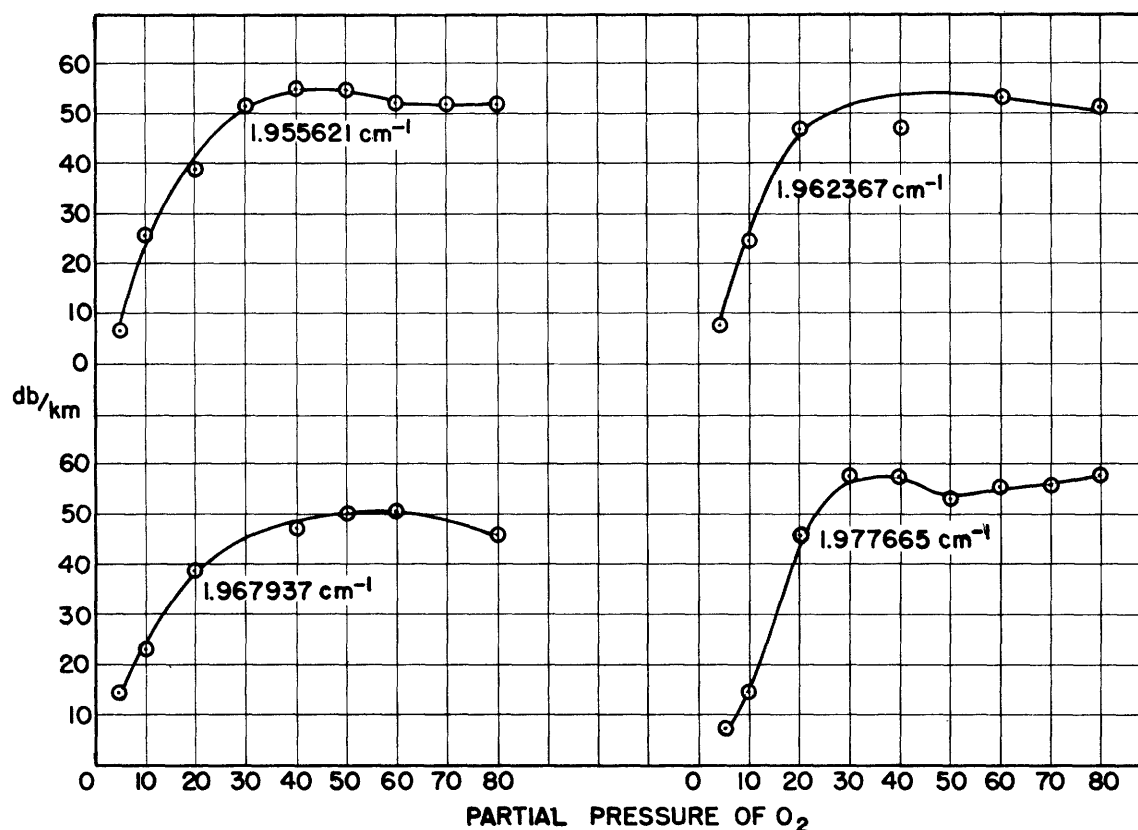


Fig. 3 Curves of absorption in oxygen-nitrogen mixtures vs.
oxygen partial pressure, taken at various frequencies.

toward the partial-pressure axis would possibly not be so great as that observed. The interval 1.950 cm^{-1} to 1.976 cm^{-1} is $.026 \text{ cm}^{-1}$ wide and a decrease in line breadth much below $.015 \text{ cm}^{-1}$ would tend to decrease the absorption in the least resonant region of 1.963 cm^{-1} . However, the $K_{-}=7$ line (1.976 cm^{-1}) and the $K_{+}=3$ line (1.950 cm^{-1}) may be closer together than we have assumed from Babcock's analysis; or the line breadth for those two lines may be different from the average line breadth of $.015 \text{ cm}^{-1}$. A variation of line breadth with rotational-energy state is certainly understandable; the possibility of such a phenomenon has been pointed out by Van Vleck and Weisskopf (9), and has been demonstrated experimentally in the case of ammonia by Bleaney and Penrose (10). It should be noted that the case of ammonia is unusual, since there are large diagonal dipole matrix elements which presumably make the line breadth a function of the rotational state. Similar elements for oxygen should be too small to consider by virtue of the hundredfold-smaller magnetic dipole moment of oxygen.

It can be readily seen from Figure 3 that dilute oxygen (~25 per cent oxygen) does behave like an absorbing gas with constant line breadth, since

the absorption becomes proportional to the oxygen partial pressure. In highly diluted oxygen, the collisions which interrupt the radiation process are predominantly those between oxygen and nitrogen molecules; so that if the anomalous behavior of the absorption in O_2-N_2 mixtures containing a high percentage of O_2 is, in fact, due to a line-narrowing phenomenon, one would be led to believe that the characteristic line breadth for oxygen absorption is smaller in the case where nitrogen is the interrupting agent than it is in pure oxygen. The difference in the line breadths might be a factor of four, but this is only a guess.

A conclusive check on the experiments would be that obtained from a comparison of the integrated absorption for various concentrations of oxygen. The integrated absorption is independent of the line breadth and must be a linear function of the number of absorbing molecules. It would seem difficult to fulfill such a requirement with data such as are given in Figure 3. However, it must be remembered that the integrated intensity may still be decreasing due to decreasing skirt absorption. In short, we have too little data for mixtures of oxygen and nitrogen to be able to apply the criterion of appropriate variation of the integrated intensity. Measurements of this type are sufficiently tedious to discourage us from carrying them out and, furthermore, observations on individual lines at low pressures seem to be more useful in developing a model for the processes taking place.

It has been pointed out above that the line breadth $\Delta\nu \cong .015 \text{ cm}^{-1}$ is less than the kinetic-theory value of $.04 \text{ cm}^{-1}$. Any further narrowing due to a preponderance of O_2-N_2 collisions, though certainly possible, is hard to visualize in any simple fashion.

It should also be noted that Bleaney and Penrose(10) found anomalous values for the collision cross sections, or line widths, in ammonia-nitrogen mixtures. The supposedly similar cross sections for ammonia-argon and ammonia-oxygen collisions determined from the line breadths are smaller by a factor of two. This large discrepancy worried these experimenters enough to cause them to remeasure the ammonia-nitrogen value, but they found no error and let the matter stand. Unfortunately, these experiments are of little value here, since the effect Bleaney and Penrose observe is in the wrong direction (i.e., they observe nitrogen broadening) and the collision cross sections are for interaction with ammonia. The point remains that in two cases, those of oxygen and ammonia, dilution of an absorbing gas with nitrogen has indicated an anomalous behavior of the nitrogen molecules.

Briefly it may be said that measurements made on pure oxygen cannot be reduced to atmospheric absorption by a simple multiplication with the fraction representing the number of oxygen molecules present. The variation of the absorption in oxygen-nitrogen mixtures is not readily understandable.

At low oxygen concentration, the absorption does vary proportionally to the partial pressure of oxygen, as might be expected. On the other hand, in mixtures with a high percentage of oxygen, the absorption becomes almost independent of the partial pressure of the oxygen over a region several line breadths wide. Qualitatively, this independence of absorption on the concentration of oxygen might be due to a variation arising from a difference between O_2-O_2 and N_2-O_2 collisions, but the phenomenon can not be quantitatively explained on the basis of available data. Further, the measurements presented here are not in good agreement with previously published experimental data. Beringer (2) found that the absorption in oxygen-nitrogen mixtures is proportional to the oxygen partial pressure. Lamont (3) measured directly the absorption in the atmosphere and found it to be about 15 db/km. On the basis of our experiments, we would predict the absorption due to oxygen in the atmosphere to be about 30 to 40 db/km.

A good deal of work remains to be done. Studies of the absorption in pure oxygen at low pressures should be carried out to determine the exact transition frequencies, any shift of frequency with pressure, any dependence of the line breadth upon rotational state, and any anomalous dependence of the line breadth on pressure. We intend to carry on further researches along these lines in this Laboratory. The data given above form an incomplete study of the absorption phenomena in oxygen, and are presented at this time so that the material already at hand might be made available, without further delay, to those interested in the problem.

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