The Absorption of Microwaves by Oxygen*

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Even though electrically non-polar, oxygen gas absorbs microwaves because the magnetic moment of the O_2 molecule interacts with electromagnetic fields. The resulting absorption is most pronounced, exceeding 10 db/km, for wave-lengths in the vicinity of $\frac{1}{2}$ cm, for then there is resonance to the spacings in the "rho-type triplet" or spin fine-structure in the $^3\Sigma$ ground state of O_2. There is also a subsidiary resonance near $\frac{1}{4}$ cm, and a non-resonant absorption at long wave-lengths due to diagonal matrix elements. The calculated values of the absorption are given in Table II and depend on the choice of the line-breadth constant $\Delta\nu$ which represents the effect of broadening by collision. Comparison is made of these theoretical results with the absorption in the $\frac{1}{2}$ cm region, observed by various experimentalists with different methods. It is concluded that 0.02 cm^{-1} is probably the best choice for $\Delta\nu/c$. The theoretical dependence of the absorption on pressure is discussed, and is particularly interesting because of the relation to the mechanism of collision-broadening and because the resonances to individual rotational lines are resolved at low pressures.

INTRODUCTION

BOTH the oxygen and nitrogen molecules are electrically non-polar. Hence at first thought, one is likely to conclude that dry, un-ionized air cannot absorb microwaves. The quantum-mechanical basis for this inference is the fact that in non-polar molecules the selection principles allow electric dipole radiation or absorption only when associated with a transition between two different electronic states of a molecule, rather than between two components of a single electronic state. Because the Bohr frequency condition makes frequency proportional to the change in energy of the molecule, switches in electronic state give resonances in the ultraviolet rather than microwave region.

The oxygen molecule, however, is paramagnetic or, in other words, has a permanent magnetic moment. Consequently it can absorb microwaves, since transitions for magnetic dipole radiation are permitted which join closely-spaced components of the ground state, and which hence give resonances in the microwave domain. Usually one thinks of absorption as arising only from electric dipoles, but it can also result from magnetic polarity, since Maxwell's equations are symmetric in E and H. To be sure, the magnetic

effect is much weaker than the electric one would be were it present, inasmuch as one Bohr magneton is about 1/100 of a Debye unit of electric polarity. However, because of the great path lengths involved in atmospheric transmission, the magnetic absorption due to oxygen is very pronounced if the wave-length is in the vicinity of $\frac{1}{2}$ cm, where there is a resonance maximum. There is also some absorption, though very much weaker, in the more conventional, longer wave-length microwave region. The purpose of the present paper is to compute the magnitude of the attenuation.

THE FINE STRUCTURE OF THE MOLECULAR SPECTRUM OF OXYGEN

The analysis of the band spectrum of oxygen shows that the oxygen molecule has a $^3\Sigma$ ground state. Since the spin quantum number S consequently is 1, and the gryomagnetic ratio $g(e/2mc)$ has a Landé factor $g=2$, the oxygen molecule carries a magnetic dipole moment of two Bohr magnetons.[1] This magnetic moment interacts with the "end-over-end" rotation of the oxygen molecule to form what the band spectroscopists call a "rho-type triplet." If K be the

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[1] For a résumé of the theory of the magnetic properties of the oxygen molecule, see pp. 262-264 and p. 266 of the writer's *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932). For the theory of rho-type triplets see H. A. Kramers, Zeits. f. Physik **53**, 422 (1929); M. H. Hebb, Phys. Rev. **49**, 610 (1936); also R. Schlapp, Phys. Rev. **51**, 342 (1937).

rotational quantum number exclusive of spin, then K is compounded vectorially with the spin S to yield a resultant inner or rotational quantum number J for the molecule which can take on the values $K-1$, K, and $K+1$. Because the oxygen nucleus is devoid of spin, the Pauli exclusion principle allows K to take on only odd values. The intervals separating states of different K are magnetically inactive, and, anyway, are so large that they would give resonances in the infra-red rather than microwave region. It is only the fine structure of the rho-type triplet, in other words the decomposition of the three states of given K but different J, which is small enough to give microwave resonances. The components $J=K-1$ and $J=K+1$ nearly coincide with each other, and differ from $J=K$ by intervals which depend on K but which, with one exception, are about 2 cm⁻¹, corresponding to a wave-length of $\frac{1}{2}$ cm. Fortunately the selection principle that J cannot change by more than one unit prevents transitions between the components $K-1$ and $K+1$ from being magnetically active, as otherwise the near coincidence of these components would lead to strong absorption in the ordinary microwave region, of the order $\lambda=10$ cm.

In our calculations it is necessary to know the spacings of the components with some accuracy. Fortunately, these have been determined by Dieke and Babcock[2] by measuring the lines of the atmospheric absorption bands of O_2 in stellar spectrograms. The resulting intervals are tabulated in the columns of Table I labelled "spectroscopic." Two sets of values are given. Those listed as "D. & B." are derived from the original article of Dieke and Babcock, while those termed "new B." incorporate the results

TABLE I. Energy intervals in the oxygen spin triplets. The intervals separating the components $J=K-1$, $K+1$ from $J=K$ are denoted respectively by $h\nu_{K-}$, $h\nu_{K+}$.

	ν_{K-}/c spectroscopic D. & B.	ν_{K-}/c spectroscopic new B.	ν_{K-}/c theory (Schlapp)	ν_{K+}/c spectroscopic D. & B.	ν_{K+}/c spectroscopic new B.	ν_{K+}/c theory (Schlapp)
$K=1$	——	——	3.962	1.872	1.873	1.878 cm⁻¹
3	2.084	2.085	2.084	1.950	1.951	1.950
5	2.011	2.012	2.012	1.981	1.986	1.988
7	1.976	1.975	1.974	2.021	2.017	2.016
9	1.949	1.949	1.946	2.045	2.041	2.039
11	1.919	1.919	1.922	(2.06)	2.063	2.061
13	1.899	1.900	1.901	(2.08)	2.083	2.081
15	1.877	1.881	1.881	2.10	2.103	2.100
17	1.864	1.862	1.861	2.12	2.124	2.119
19	1.838	1.844	1.843	(2.14)	2.150	2.137
21	1.815	——	1.824	(2.16)	——	2.156
23	1.81	1.813	1.806	2.18	2.180	2.173
25	(1.80)	1.784	1.788	(2.20)	——	2.191
$\geqq 27$	{1.78 $-0.01(K-27)$}		($-0.0084K$ $+1.985$ $+0.31/K$ $-\cdots$)	{2.22 $+0.01(K-27)$}		($+0.0084K$ $+1.993$ $-0.31/K$ $+\cdots$)

of new unpublished studies by Professor Babcock which he has kindly made available to us. He is able to improve the accuracy by more careful averaging and appraisal of the experimental data.[2] The difference compared to the earlier values is a relatively slight one, amounting in most cases to only a few thousandths of a wave number.

In other columns of Table I we include for comparison the intervals furnished by a theoretical formula of Schlapp,[3] based on the quantum mechanics of the coupling of spin to molecular rotation in a rho-type triplet. It is quite possible that the individual levels given by Schlapp's expression are more reliable than the spectroscopic values. His formula involves one undetermined constant which is so chosen as to fit the general run of experimental data in the best possible way. The separation between the components $J=0$ and $J=1$ of $K=1$ must be obtained from Schlapp's theory, for this particular interval is not obtainable from the ordi-

[2] G. H. Dieke and H. D. Babcock, Proc. Nat. Acad. Sci. 13, 670 (1927). The intervals can also be obtained from spectroscopic measurements by Badger and Mecke (Zeits. f. Physik 60, 59 (1930)) which use a laboratory rather than solar light source. However, we do not include these values in Table I, since their irregular trend with K indicates that they are probably less accurate than those of Dieke and Babcock, from which they often differ by over 0.01 cm⁻¹. Babcock's new figures are obtained by averaging over a variety of different bands having different vibrational quantum numbers in the upper state, but of course always zero vibration in the lower one, since we are interested only in the characteristics of the normal, vibrationally unexcited ground level. On the other hand, in quoting Dieke and Babcock's data, we give only their measurements on one particular band, the so-called B one ($v=1\rightarrow v=0$).

[3] R. Schlapp, Phys. Rev. 51, 342 (1937). In computing the intervals by means of Schlapp's formula for Table I, slightly different values of the constants B, μ (but not λ) have been used than in his original paper (viz. $\mu=-0.00837$, $B=1.43777$ cm⁻¹ instead of -0.008, 1.438). Mrs. Herzberg tells us that the fit with the spectroscopic data is improved by the new choice of μ, which is arbitrary. The writer is much indebted to her for supplying him with the results of the calculations with the revised constants. In applying Schlapp's formula (2), care must be exercised to take the proper branch of the radical in the particular case $J=0$, as this may involve a different numerical choice of sign for the root than for other values of J. The appropriate form of Schlapp's expression W_{K-1} for $K=1$ is $-2\lambda-\mu$, as can be verified from the basic theory, or more simply, from the fact that the multiplet intervals must vanish with the spin-orbit constants λ, μ.

nary spectroscopic data. Because of blending, perturbations, or some other reason, the spectroscopic values are not reliable for the level $K=21$. For this value of K, and also for values of K higher than about 25, the intervals are best estimated by interpolation or from theory. Intervals thus obtained, rather than by direct measurement, are inclosed in parentheses when listed in the "spectroscopic" columns of Table I.[4]

Wisely or unwisely, in our calculations of the absorption we have used the spectroscopic rather than theoretical values of the intervals, in order to tie in as closely as possible with direct experiment rather than theory. We used Dieke and Babcock's original values of the intervals, since Babcock's revised figures were not available at the time the calculations were made. As a matter of fact, the differences between the different sets

of values, including those based on Schlapp's formula, are far too small to be of consequence except at very low pressures. Thus the curves and tables which we give later in the article for the absorption at atmospheric pressure would have been changed only in a trivial way had we employed Babcock's new figures, or used the Schlapp formula. When the line-breadth constant is as high as 0.05 or 0.1 cm^{-1}, the lines overlap so much at ordinary pressures that sharp resonances are obliterated, and for these values of $\Delta\nu/c$ we have employed "rounded" intervals which are carried only to two decimals. It has nevertheless seemed advisable to give in Table I the best available estimates of the intervals, rather than just those employed in our calculations since in the future improved microwave technique may make it possible to locate individual lines with accuracy.

THE FORMULAS FOR THE ABSORPTION

The general quantum-mechanical expression for the absorption coefficient is

$$\gamma = 10^6 (\log_{10} e)\left(\frac{8\pi^3 \nu N}{3hc}\right)\frac{\Sigma_{i,j}\{|\mu_{ij}|^2 f(\nu_{ij}, \nu)\}e^{-E_j/kT}}{\Sigma_j e^{-E_j/kT}}. \tag{1}$$

Here μ_{ij} is the matrix element of the dipole moment connecting two stationary states i, j of energy E_i, E_j, respectively, while ν_{ij} is the frequency of the corresponding spectral line, given by the Bohr frequency condition $h\nu_{ij}=E_i-E_j$. The frequency of the incident radiation is denoted by ν and the number of molecules per cc by N. The factor $10^6 \log_{10} e$ is included in order that the absorption be expressed in decibels per kilometer. The factor $f(\nu_{ij}, \nu)$ may be termed the "structure-factor" governing the shape of the absorption line, and is given by the expression

$$f(\nu_{ij}, \nu) = \frac{\nu}{\pi\nu_{ij}}\left[\frac{\Delta\nu}{(\nu_{ij}-\nu)^2+\Delta\nu^2}+\frac{\Delta\nu}{(\nu_{ij}+\nu)^2+\Delta\nu^2}\right]. \tag{2}$$

Near resonance, (2) is practically identical with

$$f(\nu_{ij}, \nu) = \frac{1}{\pi}\left[\frac{\Delta\nu}{(\nu_{ij}-\nu)^2+\Delta\nu^2}\right]. \tag{3}$$

The expression (3) is the form of structure-factor commonly given in the literature, and is a good approximation when $\Delta\nu$ and $|v_{ij}-\nu|$ are both small in magnitude compared with ν. These conditions

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[4] The spectroscopic determinations of the intervals involved in Table I are based on measurements of the atmospheric bands of O_2, which arise from magnetic dipole radiation in a $^3\Sigma_g^- - ^1\Sigma_g^+$ transition. Because of the selection rules that prohibit combinations of $J=0$ with $J=0$, and of changes of J by more than one unit in dipole radiation, the state $J=0$ of $^3\Sigma_g^-$ cannot combine with any $^1\Sigma_g^+$ level, and so cannot be detected. This statement is no longer true when one allows for the possibility of electric quadrupole radiation, but whether the resulting satellite lines are strong enough to be detectable is uncertain (cf. J. H. Van Vleck, Astrophys. J. **80**, 161 (1934)). There are a few electronic states which can combine with $J=0$ of $^3\Sigma_g^-$ even in dipole radiation. Hence in principle the interval ν_{1-} should be detectable if one measured the right bands. However, the known electronic states of O_2 are very limited in number, and to date the experimental difficulties have apparently been prohibitive. For instance, the Schumann-Runge-Fuchtbauer $^3\Sigma_g^- - ^3\Sigma_u^-$ bands are in the ultraviolet, and so the dispersion has not been adequate to resolve the triplet components. The Herzberg $^3\Sigma_g^- - ^3\Sigma_u^+$ bands, though weak, probably offer more chance of success.

are well fulfilled when one deals with the absorption of visible light or infra-red. In studying the absorption of microwaves at frequencies which fall outside sharp resonances, one may encounter cases where $|\nu_{ij}-\nu|$ and even $\Delta\nu$ are of the same order of magnitude as ν. It is then necessary to use the more exact formula (2). The theory involving Eq. (2), which involves inclusion of a term omitted in the standard Lorentz theory of collision broadening, is given in a previous paper by Van Vleck and Weisskopf.[5] In this connection it should be mentioned that their results are obtained essentially by the correspondence principle, and involve the quantum-mechanical transcription of classical formulas. As pointed out to the writer by Professor Dennison, this transcription is not unambiguous, since somewhat different results are obtained according as one applies the correspondence principle directly to absorption, or to emission. With the latter method, the absorption is obtained indirectly by utilizing the Einstein relation between spontaneous radiation and absorption. Thus there is some doubt as to the correct quantal expression for the shape and structure of an absorption line. The uncertainties, however, are of such a character as to be of no consequence if the incident frequency ν and the molecular resonance frequency ν_{ij} are both small compared to kT/h. Fortunately, these conditions are abundantly fulfilled for the oxygen lines studied in the present paper.

The constant $\Delta\nu$ involved in (2) is the so-called line-breadth constant. It represents the effect of damping by collision, which is the most important cause of broadening in the microwave region. Here the wave-length is far too long for the Doppler effect or radiation-damping to have any appreciable effect on the line profile. The constant $\Delta\nu$ cannot be calculated theoretically, as the corresponding collision diameter need not be the same as the gas-kinetic one or the molecular diameter, and usually turns out much larger than the latter. Until recently, uncertainty in the value of $\Delta\nu$ has been a stumbling block in the theoretical calculation of microwave absorption. However, microwave measurements have themselves lately furnished much of the needed information on $\Delta\nu$.

Since $h\nu_{ij}=E_i-E_j=-h\nu_{ji}$ we have $f(\nu_{ij}, \nu) = -f(\nu_{ji}, \nu)$, and the contribution of a typical term i, j in (1) to the absorption is positive or negative according as the energy of the state i is greater or less than that of j. The negative contributions are often called induced emission. If the resonance frequencies are small compared to kT/h, the positive and negative terms nearly cancel. Namely, to any given term i, j in the double sum in (1), there is also a corresponding term j, i whose contribution is of opposite sign, and which would cancel the effect of i, j completely were it not for the difference in the Boltzmann factors for the states i and j. This difficulty of nearly compensating terms may, however, be avoided by using the approximation

$$\nu_{ij}e^{-E_j/kT}+\nu_{ji}e^{-E_i/kT}=\tfrac{1}{2}(h\nu_{ij}^2/kT)(e^{-E_j/kT}+e^{-E_i/kT}) \tag{4}$$

which applies when $|\nu_{ij}|\ll kT/h$. This simplification is well warranted in the application of the present paper, since the width of the rho-type triplet of oxygen is only about $1/100$ of kT/h. When (4) is employed, Eq. (1) becomes

$$\gamma = 10^6(\log_{10}e)\frac{8\pi^3\nu N}{6ckT}\frac{\Sigma_{i,j}\{|\mu_{ij}|^2\nu_{ij}f(\nu_{ij}, \nu)\}e^{-E_j/kT}}{\Sigma_j e^{-E_j/kT}}. \tag{5}$$

The advantage of using (5) rather than (1) is that all terms in the numerator of (5) are positive.

In our applications to oxygen, the index i (or j) signifies a trio of quantum numbers J, K, M (or J', K', M'), where we have $J=K-1, K, K+1$ as previously explained, and where M is the equatorial or "magnetic" quantum number associated with the space quantization of J. The energy does not depend on M, and only slightly on J. Hence in the Boltzmann factors (but not in the structure-factor given in Eq. (2)) we can make the approximation $E(K, J)=E_K$ where E_K is independent of J.

⁵ J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945); H. Frohlich, Nature **157**, 478 (1946).

The matrix elements of the magnetic moment are of the type $K'=K$, $J'=J-1$, J, $J+1$. Consequently (5) takes the specific form

$$\gamma = 10^6(\log_{10}e)\frac{4\pi^3\nu N\ \Sigma_K\{2\mid\nu_{K+}f(\nu_{K+},\ \nu)\mid\mu_{K+}{}^2+2\mid\nu_{K-}f(\nu_{K-},\ \nu)\mid{}^2\mu_{K-}{}^2+F(\nu)\mu_{K0}{}^2\}e^{-E_K/kT}}{3ckT\ \Sigma_K3(2K+1)e^{-E_K/kT}},\quad(6)$$

where ν_{K+}, ν_{K-} are defined as in Table I, and where

$$F(\nu)=\lim_{\nu_{ij}\to0}[\nu_{ij}\,f(\nu_{ij},\ \nu)]=\frac{2\nu\Delta\nu}{\pi(\nu^2+\Delta\nu^2)}.\quad(7)$$

The intensity formulas[6] of quantum mechanics appropriate to the type of vector addition involved in a rho-type triplet (Hund's case b) show that

$$\mu_{K+}{}^2=\frac{4\beta^2K(2K+3)}{K+1},\quad\mu_{K-}{}^2=\frac{4\beta^2(K+1)(2K-1)}{K},\quad\mu_{K0}{}^2=\frac{8\beta^2(K^2+K+1)(2K+1)}{K(K+1)},\quad(8)$$

where β is the Bohr magneton $he/4\pi mc$.

The first and second members of (6) represent the resonant absorption of oxygen, which is particularly important in the vicinity of $\nu/c=\frac{1}{2}$ cm. The third member gives the non-resonant or diagonal part of the absorption, which will be discussed and explained more fully below. In the Boltzmann factors, it is an adequate approximation to take $E_K=BK(K+1)$, with $B=1.44$ cm^{-1}, so that at 293°K we have $e^{-E_K/kT}=10^{-0.0030K(K+1)}$. Because of the exclusion principle, only odd values of K are involved in the summation in (6). Without appreciable error, the sum in the denominator may be replaced by the integral

$$3\int_0^\infty K\exp[-BK^2]dK=3kT/2B.$$

On the other hand, the first and second members of the numerator, must be summed in detail, and in this connection it is necessary to know the energy levels or frequency intervals accurately, since $f(\nu_{ij},\ \nu)$ is sensitive to the value adopted for ν_{ij}. We utilized the D. & B. values in Table I, which has already been discussed. Outside of the resonance region, the absorption becomes less sensitive to the values of the molecular frequencies. It is then adequate to make the centroid approximation of considering all the frequency denominators to be the same. In place of (6) one then has the very simple formula

$$\gamma=0.34\left(\frac{\nu^2}{c^2}\right)\left[\frac{\Delta\nu/c}{[2-(\nu/c)]^2+(\Delta\nu/c)^2}+\frac{\Delta\nu/c}{[2+(\nu/c)]^2+(\Delta\nu/c)^2}+\frac{\Delta\nu/c}{(\nu/c)^2+(\nu\Delta/c)^2}\right],\quad(9)$$

if $T=293°$, $p=76$ cm. Use of (9) is warranted if $\nu/c>4.5$ or <1.5 cm^{-1}. The reason that we say >4.5 rather than >2.5 is that Table I shows that one particular line ν_{1-} has a resonance wave-number of about 4 rather than 2 cm^{-1}, and so gives a peak in the absorption near 4 cm^{-1}, i.e., $\lambda=\frac{1}{4}$ cm, which will be discussed later in connection with Eq. (13).

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[6] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, 1935, New York), pp. 64-72. Translated into their notation, our quantities $\mu_{K\pm}{}^2$ are the same as their expression

$$(2\beta/\hbar)^2(2j+1)(\gamma j_1j_2j;J_1;\gamma j_1j_2j')^2\leftrightharpoons(j,\ j')$$

provided we take $j_1=1$, $j_2=K$, $j=K$, $j'=K\pm1$. Our quantity $\mu_{K0}{}^2$ is obtained from this espression by taking $j=j'$, and summing over the three components $j=K-1$, K, $K+1$.
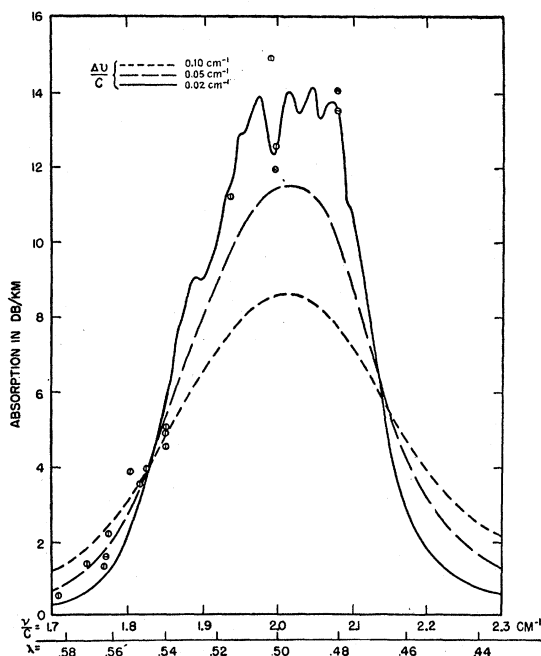
Fig. 1. The absorption, due to oxygen, of dry air at 300°K, 76 cm, for wave-lengths in the vicinity of $\frac{1}{2}$ cm. The curves are calculated theoretically for various values of $\Delta\nu/c$, as indicated. The experimental points are by Beringer. The vertically, horizontally, and diagonally crossed circles refer respectively to measurements made on pure O_2, on O_2-N_2 mixtures with 50 percent O_2, and on 20 percent O_2. The equivalent values for air are obtained from the experimental data by assuming that the cross section is the same for O_2-N_2 and O_2-O_2 collisions, so that the absorption at constant total pressure is directly proportional to the oxygen content.

THE NON-RESONANT OR DIAGONAL PART OF THE ABSORPTION

The third term of (6), i.e., the term with factor $F(\nu)$ represents the non-resonant part of the absorption. It results from the fact that the matrix for the magnetic moment of the oxygen molecule has diagonal matrix elements. Perhaps we have previously given the impression in this paper that the magnetic absorption of oxygen consisted entirely of lines in the vicinity of $\lambda = \frac{1}{2}$ cm, with a satellite at $\frac{1}{4}$ cm. Actually, however, there are also lines whose resonance frequency is zero, and which we hence call non-resonant. They arise from the fact that the matrix for the spin magnetic moment of the oxygen molecule has diagonal elements in addition to the non-diagonal ones which are responsible for the resonance at $\frac{1}{2}$ cm. The diagonal and non-diagonal elements come, respectively, from

the projections of the spin vector $\mathbf{S}$ parallel and perpendicular to the resultant angular moment vector $\mathbf{J}$ about which $\mathbf{S}$ precesses. The diagonal members are the quantum analog of a constant term in a classical Fourier expansion. One may wonder how absorption can arise from a constant rather than variable moment. The answer is that the constancy is spoiled by the interruptions due to collisions, and the radiative effect is caused by the pulses attendant to the realignments of collision. The mechanism of absorption due to the diagonal elements is in many ways similar to that in Debye's[7] well-known model of absorption and dispersion of a molecule at radio-frequencies due to redistribution of molecular dipoles by collisions. In fact, when a slight, well-warranted approximation is made, the third member of (6), which is the diagonal effect, has precisely the same form as Debye's expression for the absorption, viz.,

$$\gamma = 10^6(\log_{10}e)\left(\frac{8\pi^2\nu^2N\mu^2}{3kTc}\right)\frac{\Delta\nu}{\nu^2+\Delta\nu^2}. \quad (10)$$

The approximation consists in taking $\mu_{K0}^2 = 8\beta^2\cdot(2K+1)$ instead of using the more accurate value given by (8). Since K is large for the great bulk of the rotational states, this simplification is entirely allowable, and makes the sum cancel from numerator and denominator in the third member of (6). This part then becomes identical with (10) provided the square μ^2 of the dipole moment is given the value

$$\mu^2 = g^2S(S+1)\beta^2/3 = 8\beta^2/3, \quad (11)$$

where g is the Landé factor and S is the spin quantum number. The factor $\frac{1}{3}$ appears in (11) because on the average one-third of the total mean square moment is of the diagonal variety, the other two-thirds being consumed by the non-diagonal type. When (11) is utilized, it is found that the numerical value of the expression (10)

[7] P. Debye, Polar Molecules (Chemical Catalog Company, New York, 1929), Chap. V. Debye's derivation of (10) was a classical one. A proof of (10) by means of quantum rather than classical theory, and intended primarily for a magnetic rather than electric moments, has been given by C. J. Gorter and R. de L. Kronig, Physica 3, 1009 (1936) and by Kronig, ibid. 5, 65 (1938). See also W. Kauzmann, Rev. Mod. Phys. 14, 12 (1942); Van Vleck and Weisskopf, reference 5.

at 293°, 76 cm becomes

$$\gamma = 0.34 \left(\frac{\nu}{c}\right)^2 \left[\frac{\Delta\nu/c}{(\nu/c)^2 + (\Delta\nu/c)^2}\right] \text{db/km.} \quad (12)$$

Equation (12) gives the principal part of the oxygen absorption if the wave-length is greater than about 1.5 cm.

It should be emphasized that the distinction between resonant and non-resonant absorption is, in a certain sense, a purely artificial one. The diagonal elements can be made of the non-diagonal variety, but of course with zero frequency, by choosing the axis of quantization perpendicular rather than parallel to the incident field. Then the matrix elements of magnetic moment parallel to the field are of the type $\Delta M = \pm 1$ rather than $\Delta M = 0$, where M is the equatorial or magnetic quantum number associated with the axis of quantization. Thus non-resonant absorption is equivalent to resonant absorption when the natural frequency in the latter is made to approach zero as already tacitly implied in (7). This equivalence is secured only when the Lorentz expression for the line profile is modified in the fashion explained by Van Vleck and Weisskopf.[5] Without the revision, the Lorentz result does not reduce to that of Debye and Kronig in the limiting case of zero frequency. Fortunately the diagonal and non-diagonal effects can now be treated by a unified, consistent formalism.

Numerical Values of the Absorption—Comparison with Beringer's Experiments

Before a numerical comparison can be made of the theoretical formulas with experiment, some choice must be made as to the value of the collision parameter $\Delta\nu$. When the theory was first developed by the writer[8] in 1942, no microwave data were available, and the best that could be done was to try to estimate $\Delta\nu$ from measurements on the widths of absorption lines in the infra-red region. Furthermore, the infra-red data were not on oxygen itself, inasmuch as the oxygen molecule is inactive because it is electrically non-polar. The best procedure available was to extrapolate from the infra-red
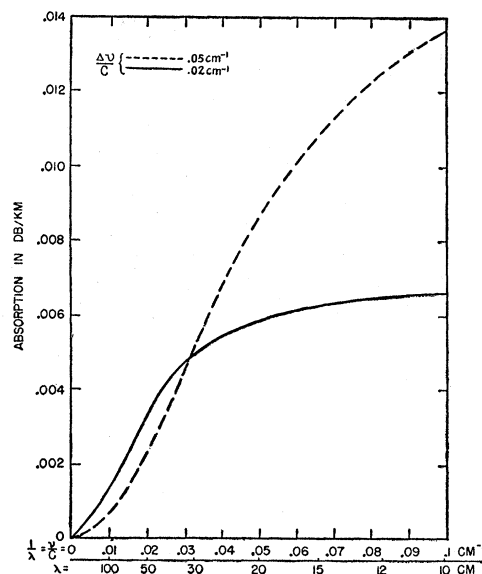

FIG. 2. The absorption, due to oxygen, of dry air at 293°K, 76 cm for wave-lengths greater than 10 cm.

spectra of CO and other molecules somewhat related to O_2. In this fashion the writer concluded[8] that the most reasonable choice for $\Delta\nu/c$ was 0.1 cm^{-1}. Subsequent microwave measurements made on O_2 by Beringer[9] show unequivocally that actually $\Delta\nu/c$ is quite a little lower and is probably between the limits 0.02 and 0.05 cm^{-1}. It is not surprising that the earlier estimates based on infra-red work should prove to be somewhat in error, for infra-red determinations of the width of a spectral line require very high resolving power and involve difficult corrections for slit width, not to mention the fact that the observations are not made on oxygen directly.

Figure 1 shows the calculated absorption as a function of frequency in the resonance region around $\lambda = \frac{1}{2}$ cm. Beringer's experimental data[9] are also included for comparison, and are indicated by the various points. His measurements on pure or 50 percent O_2 are reduced to "air equivalent" by assuming that at given total pressure the absorption is directly proportional to the concentration of oxygen. This procedure appears legitimate, since Beringer's data show that the collision cross section is substantially the same for O_2-N_2 and O_2-O_2 impacts. For

[8] For details see pp. 10–12 of M.I.T. Radiation Laboratory Report 43–2.

[9] R. Beringer, Phys. Rev. 70, 53 (1946).

TABLE II. Absorption of air, due to oxygen, for various values of the line-breadth constant Δν.

Δν/c = ν/c	0.01 cm⁻¹ γ	0.02 cm⁻¹ γ	0.05 γ	0.10 γ
0.1 cm⁻¹	0.0033 db/km	0.0066 db/km	0.014	0.017
.33	.0036	.0072	.018	.033
.67	.0045	.0089	.022	.044
.80	.0052	.010	.026	.051
1.0	.0072	.014	.036	.071
1.3	.017	.033	.083	.17
1.5	.038	.077	.192	.38
1.6	.070	.141	.35	.70
1.7	.166–0.171	.32	.74	1.26
1.77	.66–0.78	1.06	1.83	2.41
1.8		1.99		3.1
1.85	4.8–6.4	5.09–5.5	5.4	4.9
1.90		8.7–9.9		6.9
1.95		12.0–13.5		
2.00	11.4–15.5	12.9–14.1	12.0	8.9
2.05		13.9–14.8		
2.08	11.9–14.9		10.7	8.1
2.10		9.5–13.1		
2.15		5.0	5.7	5.8
2.2		1.70	3.3	4.1
2.3		.51	1.2	2.08
2.5	.096	.19	.48	.95
5.0	.0146	.03	.073	.146

further discussion of this subject and other questions relative to the experimental measurements, the reader is referred to Beringer's paper. Figure 1 shows that his data are scarcely accurate enough to decide between $\Delta\nu/c = 0.02$ and 0.05 cm⁻¹ but that 0.1 cm⁻¹ would be definitely too high. It is interesting to note that at $\nu/c = 1.83$ cm⁻¹ the various points cross, so that at this particular wave-length the absorption is almost independent of the value chosen for the line breadth. Possibly this feature might be useful in calibrating apparatus in which a constant of proportionality in the absorption is otherwise undetermined.

The wobbles in the curve for $\Delta\nu/c = 0.02$ cm⁻¹ are caused by the fact that at certain particular wave-lengths there is close resonance to some individual rotational state. This effect does not show up at 0.05 or 0.1 cm⁻¹, as the lines are then so broad that they overlap, whereas at 0.02 cm⁻¹, one has an incipient resolution of the contributions of the different rotational states. By working with low pressures and well-established frequencies, it should ultimately be possible to resolve this fine structure.

Figure 2 gives the absorption at wave-lengths greater than 10 cm. In this region, practically all of the contribution to the absorption comes from the diagonal or non-resonant effect, given by (12) or the third member of (6). The attenuation in this long wave-length region is too small to be of any consequence unless the path is very

long. This statement is true regardless of the choice of $\Delta\nu$. At given incident frequency ν, the value of $\Delta\nu$ which maximizes the expression (12) is $\Delta\nu = \nu$, and the resulting upper limit to the attenuation is 0.17/λ db/km.

Figure 1 does not extend to short enough wavelengths to show the minor but sharp resonance in the vicinity of $\lambda = \frac{1}{4}$ cm, which comes from the interval ν_{1-} separating the components $J = 0$ and $J = 1$ of $K = 1$ (cf. Table I). The corresponding peak does, however, appear in Fig. 2 of the following paper, where the absorption due to O_2 and H_2O is compared. The formula for the absorption due to the resonance near $\frac{1}{4}$ cm is

$$\gamma = 0.048\left[\frac{\Delta\nu/c}{(\nu - \nu_{1-})^2/c^2 + (\Delta\nu/c)^2}\right]. \quad (13)$$

As already mentioned, ν_{1-} cannot be determined spectroscopically, and can only be estimated from Schlapp's theoretical formula. The latter gives $\nu_{1-}/c = 3.96$ cm⁻¹, a value which is probably correct to within a few tenths of a cm⁻¹. Oscillators of short enough wave-length to detect this resonance do not exist at present, but with the present rapid development of microwave technique, it should presumably be observable in the not too far distant future.

In Table II we show the calculated absorption numerically rather than graphically. The numerical values in this table are slightly different from those in Fig. 2, since this figure is drawn for a temperature of 300° rather than 293° in order to conform to the approximate temperature of Beringer's experiments. The increase of the temperature from 293 to 300°K reduces the absorption by a factor[10] approximately $(293/300)^2$. It

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[10] The proportionality to $1/T^2$ is only approximate, and arises because (6) contains the factor N as well as $1/T$ explicitly, and because for a given the ratio of the sums in the numerator and denominator of (6) is rather insensitive to T as long as the wave-length or line-breadth is such that several lines contribute appreciably to the absorption. Where the absorption is mainly due to one line of excitation energy E_K, there is an additional factor $(1/T)e^{-E_K/kT}$ inasmuch as the sum in the denominator of (6) is nearly proportional to T. For instance, the absorption in the vicinity of $\frac{1}{4}$ cm given by (13), is caused by the state $K = 1$ for which $E_K/kT \ll 1$; the proportionality here is hence to $1/T^3$ rather than $1/T^2$. All these statements are on the supposition that $\Delta\nu$ is fixed. Kinetic theory indicates that at constant pressure $\Delta\nu$ should be proportional to $1/T^{1/2}$, but this effect can, of course, be considered only after $\Delta\nu$ has been located. In the many-line case it would make the absorption proportional to $1/T^{3/2}$ at resonance, and to $1/T^{5/2}$ well away from resonance.

will be noticed that for small values of $\Delta\nu/c$ in Table II, the absorption is given only within certain limits. This is because the exact values of the absorption lines are not known experimentally with high precision, and with narrow line-breadths, the exact amount of resonance to a particular doublet belonging to some particular rotational state is, of course, sensitive to the precise values of the resonant wave-length. In their original paper, Dieke and Babcock usually gave their intervals to 0.001 cm^{-1}, but Professor Dieke tells us it is doubtful whether they are more accurate than 0.01 cm^{-1}. The new figures of Babcock are more exact, probably having an accuracy, he tells us, of two thousandths of a cm^{-1},—at least this is suggested by the consistent good agreement with the Schlapp formula. An uncertainty of 0.01 cm^{-1} is sufficient to admit the possibility of a given applied fre-

quency being exactly at resonance with a given rotational line in the $\frac{1}{2}$ cm region, or being midway between two adjacent rotational lines. These two extremes represent, so to speak, the "most resonant" and "least resonant" possible behaviors if the frequencies are not accurately known, and have been used in constructing the upper and lower limits in Table II. If the line-breadth is more than about 0.05 cm^{-1} or so, the lines overlap so much that the resonances to the individual lines are ironed out. They also disappear if one is not in the resonance region, or if the applied frequency is not well stabilized, so that effectively a sort of average frequency over an interval is used. In drawing Fig. 1, we have not attempted to show the curve for $\Delta\nu/c = 0.01$ cm^{-1}, because the wobbles are too great. In obtaining the curves for $\Delta\nu/c = 0.02$ and 0.05 it has been assumed that Dieke and Babcock's original values
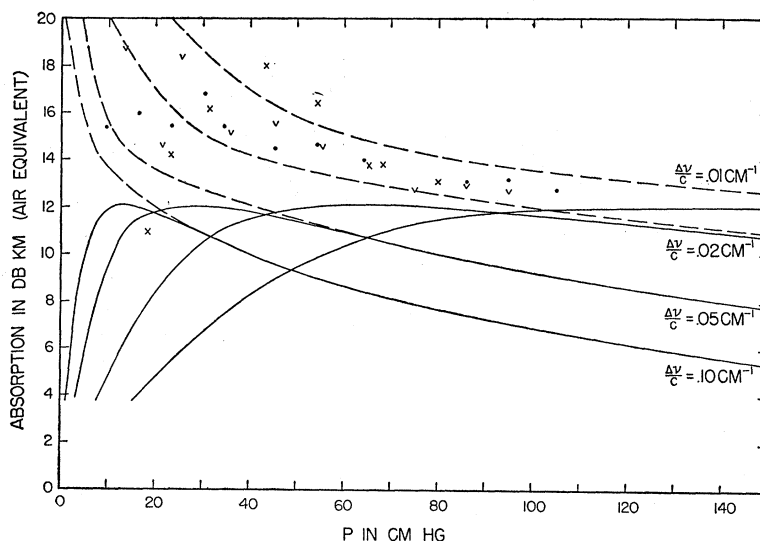

Fig. 3. The dependence of absorption on pressure at $\nu/c = 2.08$ cm^{-1}, $\lambda = 0.481$ cm. The ordinates are so normalized as to be proportional to the absorption per oxygen molecule, and give the "air-equivalent absorption" which is obtained by multiplying the measured absorption by the ratio of the partial pressure of the oxygen in the actual atmosphere to the partial pressure of the oxygen in the experiment. The solid circles, check marks, and crosses refer, respectively, to measurements made by Beringer on dried tank ("pure") O_2, mixtures of O_2-N_2 with 50 percent O_2, and mixtures with 19 percent O_2. The curves are calculated from theory under the assumption that $\Delta\nu/c$ is proportional to the total pressure; the values of $\Delta\nu/c$ with which the various curves are labelled are those applicable at 76 cm. The divergence between the solid and dashed curves indicates approximately the uncertainty in the calculation due to the fact that the resonance frequency of the line nearest coincidence with the incident frequency is not known with precision. The "on-resonance" case shown by the dashed curves, assumes that $\nu_{3-}/c = 2.08$, while the "off-resonance" case, illustrated by the solid curves, supposes that $\nu_{3-}/c = 2.09$ cm^{-1}. A line with $K = 13$, as well as the one at $K = 3$, may cause resonance, but for simplicity it is assumed throughout that $\nu_{13+}/c = 2.09$. According to Babcock's latest figures, ν_{3-}/c is 2.085 cm^{-1}.
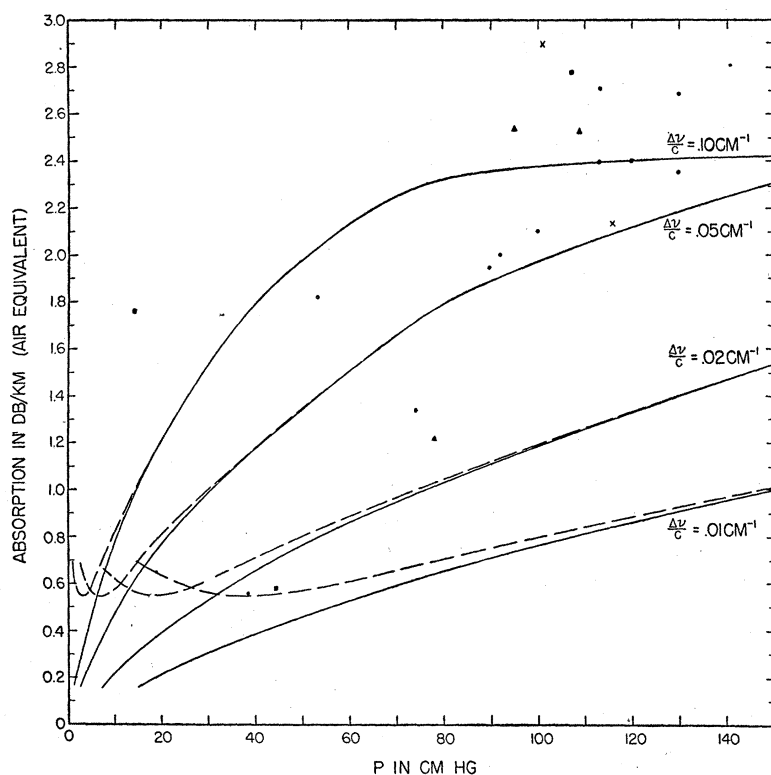
FIG. 4. The dependence of absorption per molecule on pressure at $\nu/c = 1.77$ cm^{-1}, $\lambda = 0.565$ cm. The normalization of the ordinates to the "air-equivalent" absorption and the significance of the $\Delta\nu/c$ labellings are explained in the caption for Fig. 3. The solid circles and squares are Beringer's runs on tank O_2, while the triangles and crosses are for mixtures approximately 50 percent O_2. The solid and dashed curves are for $\nu_{27-}/c = 1.78$ and 1.77 cm^{-1}, respectively; both assume $\nu_{29-}/c = 1.79$.

are reliable (except that certain irregularities have been smoothed out, as noted in connection with Table I). If the error in the experimental measurements of the frequency intervals amounts to 0.01 cm^{-1}, the positions of the minor peaks and valleys near the maximum in Fig. 1 cannot be trusted.

It is instructive and interesting to graph the absorption per molecule as a function of pressure at a given wave-length. Substantially this is done in Figs. 3 and 4, but in order to have an ordinate which is not an extremely small quantity we use for the vertical scale not the absorption of a single molecule, but rather the "air-equivalent absorption." By this is meant the attenuation in db/km which would result if one had the same number of oxygen molecules per unit volume as actually present in ordinary air, but kept the absorption per molecule the same as that observed experimentally for the pressure in question. In other words, the absorption which is plotted is the actual measured absorption multiplied by $0.21(76/p_{O_2})$, where p_{O_2} is the partial pressure of the oxygen. The curves of the

type shown in Figs. 3 and 4 are informative because they exhibit the effect of the variation of $\Delta\nu$ with pressure, and are sensitive to the position of the resonance frequency, as well as to the value of $\Delta\nu$. In drawing the curves it is assumed that $\Delta\nu$ is proportional to the total pressure, and each curve corresponds to a particular value of the line-breadth parameter. A direct proportionality of $\Delta\nu$ to the pressure is required by the ordinary Lorentz theory of collision damping such as we have assumed throughout. We should, however, mention that there is some experimental evidence[11] that in certain polar gases $\Delta\nu$ is proportional to $p^{\frac{1}{2}}$. Also some of the complicated and refined theories[12] of line-broadening developed by various authors indicate that $\Delta\nu$ need not necessarily always be linear in p, but the predicted deviation from linearity is of the opposite type from that required by a proportionality to $p^{\frac{1}{2}}$. On the

[11] For summary of the evidence and references see W. M. Brooks, Harvard Meteorological Studies, No. 6, pp. 46-47.
[12] H. Margenau, Phys. Rev. 48, 755 (1935); E. Lindholm, Arkiv for Matematik, Astronomi och Fysik, 32A, no. 17 (1945); M. Foley, Phys. Rev. 69, 616 (1946).

whole, we are inclined to believe that for our purposes it is probably a sufficient approximation to take $\Delta\nu$ proportional to p. With a non-linear dependence of $\Delta\nu$ on p, the curves would be different from those shown in Figs. 3 and 4, and when accurate experimental data become available, they should shed interesting light on this question.[13] The scatter of the Beringer data is too large to test the fine details of the theory, as is clear from the dispersion of the various experimental points in Figs. 3 and 4. Possibly insufficient stabilization of the frequency, with resulting drifting off and on resonance from one run to another accounts for some of the scatter of the absorption measurements, especially those at low pressures which are particularly difficult because the absorption is so small. When the pressure is reduced, the value of $\Delta\nu$ decreases, and the resonance phenomena become more pronounced. This is manifested by the forking of the curves in Figs. 3 and 4. In drawing these curves, instead of trying to use exactly the spectroscopic intervals of Dieke and Babcock, we have assumed that there is uncertainty amounting to 0.01 cm^{-1} or thereabouts, so that we cannot tell whether there is exact resonance to a particular rotational state or whether the incident frequency is midway between two resonances, a situation which we call "off resonance." If the pressure is sufficiently high, the values of the absorption calculated on the basis of maximum and minimum resonance practically coincide, but if the pressure is reduced enough, the two limits diverge, as evidenced by the forking of the curves. Although Beringer's points scatter too much to fix definitely which curve is the correct one, they do confirm the different trends of the absorption with pressure at wave-lengths near to and well removed from resonance. These two cases are exemplified by Figs. 3 and 4, respectively, and represent regions, where, on the whole, the attenuation per molecule tends, respectively, to decrease and increase with increasing pressure. The different behavior at different wave-lengths may be understood qualitatively as follows. If one had a single resonance line, of frequency ν_{ij}, the significant factor in the expression for the absorption would be given by Eq. (3) provided $\Delta\nu$ and $|\nu - \nu_{ij}|$ are small compared to ν. Since $\Delta\nu$ is proportional to p in the Lorentz theory, the attenuation should hence be inversely proportional to pressure in the center of the line, where $|\nu - \nu_{ij}| \ll \Delta\nu$, and directly proportional in the wings, where $|\nu - \nu_{ij}| \gg \Delta\nu$. Actually one has a mixture of various lines, and the situation is consequently more complicated, but the broad outlines of the behavior can be described by the "one-line" formula.

COMPARISON WITH OTHER EXPERIMENTAL WORK

So far we have quoted only the experimental measurements by Beringer. In 1944, Mueller[14] made a series of observations on the propagation in air of microwaves having a wave-length $\lambda = 0.625$ cm. He found no measurable deviation of the attenuation from that predicted by the inverse square law. This sets an upper limit on the absorption coefficient γ, since with a detectable γ, the transmitted energy should depend on distance in the fashion $(1/r^2)10^{-10\gamma}$. From this type of evidence, and also from unpublished studies of transmission by a wave-guide, he concluded that γ must be less than 0.09 db/km. Since the theoretical value of γ at 0.625 cm is $6.5(\Delta\nu/c)$, Mueller's measurements seem to demand that the line-breadth constant $\Delta\nu$ not exceed 0.014 cm^{-1}, which is lower than the range of values yielded by Beringer's investigations. The cause of this disagreement is not clear. The experiment which Mueller performed requires high sensitivity; the value 0.09 db/km corresponds to a reduction of only 0.8 percent in the transmitted signal over the quarter mile path which he used. He gauged his minimum detectable departure from the inverse square law by the root mean square deviation of his

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[13] Theoretically, the effect of overlapping collisions studied by Margenau (reference 12) and others enters mainly at high pressures, and so is more likely to manifest itself if the pressure is raised above atmospheric, whereas in the study of individual resonances, the most interesting experiments are at low pressures where the Lorentz assumptions are probably adequate. Some interesting experimental evidence that $\Delta\nu$ is proportional to p over a wide range of pressure may be cited. Namely, the absorption found by Townes and Merritt for water vapor at a pressure of 0.1 mm agrees gratifying well from that calculated under the assumption of such proportionality from the measurements of Becker and Autler at atmospheric pressure. This point is discussed in more detail in the following paper.

[14] G. E. Mueller, Bell Lab. Rep. MM-44-160-150.

readings from the mean. This procedure clearly does not allow for systematic errors if present. Mueller informs the writer that perhaps it is allowable to raise his upper limit to 0.13 db/km, corresponding to a line breadth $\Delta\nu/c = 0.02$ cm^{-1}. This is just compatible with the lowest value of $\Delta\nu/c$ which seems reasonable in the light of Beringer's experiments, although a sharp delineation of the least admissible $\Delta\nu$ is not possible.

Dicke, Beringer, Kyhl, and Vane[15] have made measurements on the total absorption due to the oxygen in the earth's atmospheric layer, by an ingenious radiometer method described in detail in their paper. The wave-lengths (1, $1\frac{1}{4}$, $1\frac{1}{2}$ cm) employed in these experiments are so far from resonance that the effect is weak, and hard to determine with precision. Their results do, however, seem to indicate that $\Delta\nu/c$ is of the order 0.02 cm^{-1}. Specifically, the values of $\Delta\nu/c$ required to fit their measurements at 1, $1\frac{1}{4}$, and $1\frac{1}{2}$ cm are, respectively, 0.025, 0.020, and 0.017 cm^{-1}.

In the combined light of the experiments by Beringer, by Mueller, and by Dicke and collaborators, 0.02 cm^{-1} is probably the most reasonable present choice for $\Delta\nu/c$, and the corresponding column of Table II probably represents the best estimate of the amount of atmospheric absorption due to oxygen.

At Massachusetts Institute of Technology measurements on the oxygen absorption are in progress which, because of improved frequency stabilization, are more refined than any previously attempted. Only a preliminary report of the results has been published,[16] and so we shall not make any attempt to compare the theory with them in any detail. The absolute value of the absorption, according to these new measurements, seems to indicate a line breadth $\Delta\nu/c$ $= 0.04$ cm^{-1}. On the other hand, there are fluctuations in the attenuation when the wavelength is changed which are understandable only if $\Delta\nu/c \leqq 0.02$ cm^{-1}. Otherwise the resonances to individual lines responsible for wiggles in our Fig.

1 would not be detectable. The new work does not extend to pressures below 40 cm and so cannot test curves of the type shown in our Figs. 3–4. We should caution that it should not be regarded as highly surprising if the detailed shape of the absorption curve is somewhat different from that calculated by means of our formulas. They are based on the structure factor (2), which in turn presupposes that the collisions are of infinitely short duration. Actually, impacts are not of this idealized character. There is a wealth of literature which tries in one way or another to allow for gradual and overlapping collisions. One of the most recent and comprehensive papers on this subject is that by Lindholm.[12] The more elaborate theories, however, involve undetermined constants associated with the character of the intermolecular forces, and also lead to exceedingly complicated analytical expressions for the line shape. To calculate the final result when there is a plethora of overlapping lines would hence be quite laborious, and so until the experimental data become very accurate and comprehensive, it seems best to use formulas based on the limiting Lorentz concept of infinitely short collisions, leading to the simple structure factor (2). Ultimately, however, microwave measurements, should be the method *par excellence* of testing refined theories of pressure broadening, and obtaining light on related questions concerning the nature of collisions, intermolecular forces, etc. Obviously the theory can be tested far more readily and comprehensively in the microwave region than in the optical domain where the line-breadth is so much smaller compared to frequency.

In closing we would like to emphasize that on the whole the agreement between theory and experiment must be regarded as exceedingly gratifying. Beringer measured absolute values without an undetermined calibration constant, and still the discrepancy between theory and experiment is not more than ten percent or so. The situation is thus quite different from that encountered in many measurements of the absorption coefficients of gases in the infra-red region, which have often disagreed with theory by a factor 10 or so.

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[15] R. H. Dicke, R. Beringer, R. L. Kyhl, and A. B. Vane, Phys. Rev. **70**, 340 (1946).

[16] See experiments by Meng, Ingersoll, and Strandberg summarized on p. 19 of Final Report under Contract OEMsr-262, NDRC Div. 14, Research Lab. of Electronics, M.I.T.