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The Absorption of One-Half Centimeter Electromagnetic Waves in Oxygen*

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The absorption of electromagnetic waves in the one-half cm wave-length range has been measured for O_2 and O_2-N_2 mixtures as a function of pressure. The apparatus employs a klystron oscillator, crystal-rectifier frequency-multiplier, wave guide absorption path, and crystal detector. The measured values are in agreement with the theory of Van Vleck both as regards the absolute value of the absorption (which is as great as 67 db/km at the band center for pure O_2 at a pressure of one atmosphere) and the dependence on pressure.

THE development of radiofrequency sources and techniques in the centimeter wave-length range has made possible the observation of gaseous resonance phenomena of considerable interest in molecular structure.[1] In addition there is an engineering interest in these processes since they affect the propagation of centimeter waves in gaseous media. The present paper is a part of studies concerned with the absorption of atmospheric gases in their relation to the development and use of microwave radar.

The $\frac{1}{2}$ cm O_2 absorption band was investigated theoretically in 1942 by Van Vleck.[2] The magnetic dipole moment of the $^3\Sigma$ ground state of O_2 couples with electromagnetic waves to give (a) a band of resonant absorption lines in the region of 2 cm^{-1} corresponding to the rotational transitions $J \rightarrow J \pm 1$ in a large number of spin triplets thermally excited at room temperatures and (b) a non-resonant absorption band corresponding to $\Delta J = 0$, arising because the lifetime of the states against collision is of the order of the incident wave periods. The absorption coefficients of both of these contributions were calculated with a single undetermined parameter: the lifetime or line breadth[3] of the excited states ($\Delta\nu/c$ in cm^{-1}). The experiments reported here were carried out in 1944[4] to determine this line breadth.

EXPERIMENTAL APPARATUS

The experimental arrangement consisted of a source of $\frac{1}{2}$-cm radiation, and absorption path into which gas mixtures could be introduced, and a detector of the transmitted radiation. Changes in the detected signal were measured to determine the absorption when gases were introduced. For the most part this apparatus was an obvious extension of techniques developed in this laboratory for somewhat longer wave-lengths.

The source of $\frac{1}{2}$-cm radiation was a silicon-tungsten crystal detector operated as a generator of the second harmonic of signals produced by a 1-cm oscillator. These 1-cm signals were introduced into the crystal *via* a coaxial line and the $\frac{1}{2}$-cm harmonic was extracted with a wave guide circuit. This is shown in Fig. 1. The plunger and sliding "line-stretcher" are adjustments for maximizing the radiation of $\frac{1}{2}$-cm power into the wave guide. The chokes in the coaxial line prevent $\frac{1}{2}$-cm signals from entering the oscillator tube. The efficiency of these harmonic generators (available $\frac{1}{2}$-cm power ÷ available 1-cm power) was at most 10 percent.

The oscillator tubes were designed and built by H. V. Neher, G. A. Hobart, and C. Z. Nawrocki in this laboratory.[5] They were reflex klystrons operating with accelerator voltages in the range of 2 kv, and were similar, except for oscillation frequency, to the type A-5022A klystrons later manufactured by the Radio Corporation of America. In all, four tubes were used to cover the wave-length range 0.96 cm to 1.25 cm. The accelerator, focusing, reflector, and heater volt-

* This paper is based on work done for the Office of Scientific Research and Development under contract OEMsr-262 with Massachusetts Institute of Technology.
[1] For example, the NH_3 resonance: C. E. Cleeton and H. H. Williams, Phys. Rev. **45**, 234 (1934).
[2] Radiation Laboratory Report 43-2 (April 27, 1942) and Radiation Laboratory Report 664 (March 1, 1945).
[3] The line breadth $\Delta\nu$ $sec.^{-1}$ used here is one-half of the total line breadth at half-maximum.
[4] Radiation Laboratory Report 684 (January 26, 1945).
[5] H. V. Neher, Radiation Laboratory Report IV-8S (March 1, 1942).

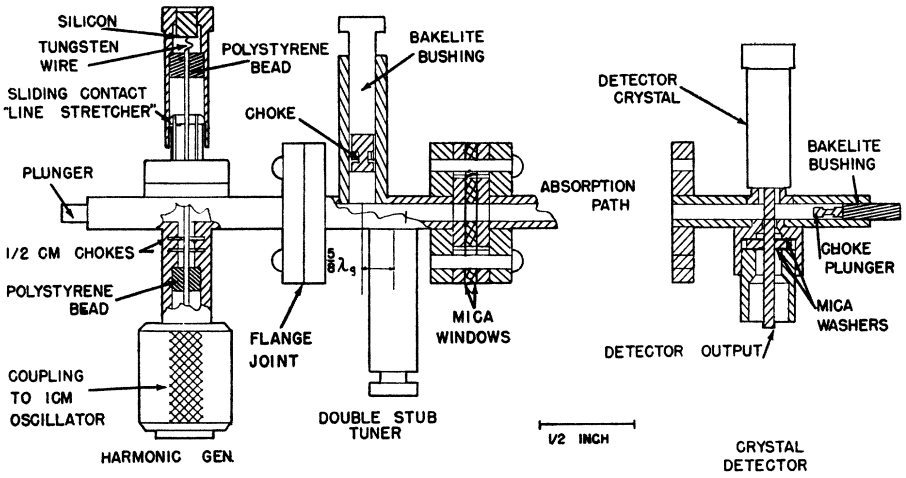

FIG. 1. Details of components of the absorption apparatus.

ages were derived from an electronically regulated power supply of conventional design. With ordinary precautions the power output from a tube (2 to 10 milliwatts) was stable to about 0.1 percent and the oscillation frequency was stable to about one part in 2000 over short (one-minute) time intervals.

The absorption path was a 6.19-meter length of rectangular, coin silver, wave guide[6] of internal dimensions 0.086 inch$\times$0.180 inch. It was provided with a double mica window at each end (see Fig. 1). Joints were waxed. A small hole in the side of the wave guide permitted evacuation and the introduction of gas from a system including manometers, storage flasks, and a commercial fore-pump.

The detector of the transmitted radiation was a silicon-tungsten crystal in a coaxial cartridge which was mounted in a wave guide circuit provided with adjustments for maximizing the detected signal. These crystals were assembled of boron-doped silicon slabs (0.003 percent Boron), prepared by M. Fox and C. S. Pearsall[7] in this laboratory, and sharply pointed 0.0015-inch tungsten wires (electrolytically etched points, 1 min. in 10 N KOH at 6 volts a.c.). The wire was formed into a U shaped spring, the point brought into contact with the silicon, pressed against it with a force corresponding to a 0.001-inch spring deflection, and the unit set permanently in that position. No tapping was used.

A wave meter, consisting of a micrometer driven plunger in round wave guide (TE_{11} mode) of known diameter (0.1495 inch) was used to measure the $\frac{1}{2}$-cm wave-lengths λ. This was mounted behind the detector and tuned to successive resonances indicated by zero detector signal. These are spaced $\lambda g/2$ apart in plunger displacement, where $\lambda g=\lambda/[1-(\lambda/\lambda c)^2]^{\frac{1}{2}}$ and $\lambda c=1.706\times$(diameter) for the TE_{11} mode.[8]

The $\frac{1}{2}$-cm source was modulated with a 1000-cycle/sec. oscillator (20 percent modulation) to produce an audiofrequency detector output. This was done because the d.c. output from a crystal detector contains very much larger noise fluctuations than does the output at audiofrequencies. The 1000-cycle/sec. detected signal was amplified in a three-stage triode amplifier of conventional design followed by another ampli-

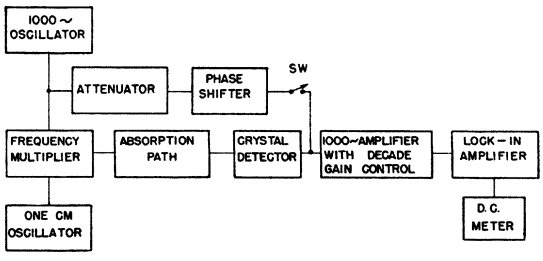

FIG. 2. Schematic diagram of the absorption apparatus.

[6] Manufactured by Horton-Angell Company, Attleboro, Massachusetts.

[7] M. Fox, C. S. Pearsall, and V. Powell, Radiation Laboratory Report 501 (December 21, 1943).

[8] S. Ramo and J. R. Whinnery, *Fields and Waves in Modern Radio* (John Wiley and Sons, Inc., New York, 1944), page 403.

fier having a coherent or "lock-in" mixer as the output stage. Such mixers are sensitive to a very narrow band of signal frequencies (about 5 cycle/sec. wide in this case), and so the noise background is reduced. The mixer output was measured with a d.c. milliammeter.

EXPERIMENTAL METHOD

The experimental arrangement is shown in Fig. 2. It operates as follows: with *SW* open the meter reading is proportional to the $\frac{1}{2}$-cm power incident on the detector. Denote this reading by e. When absorbing gas is introduced, the meter reading changes by an amount Δe, proportional to the absorption and to the original incident power. Thus $\Delta e/e$ is a measure of the absorption.

In practice the deflection Δe is magnified by closing *SW* and adjusting the phase and amplitude of the 1000-cycle/sec. balancing signal for zero output reading. The amplifier gain is then raised by a known factor and Δe is magnified by this factor. The precision to which $\Delta e/e$ can be measured is determined by spontaneous fluctuations, about 0.1 percent for the apparatus described. These fluctuations were largely attributed to tube and circuit noise present because of the high gain of the amplifier system which was necessary because of the low efficiency of the harmonic generator and the large ohmic losses in the wave guide path (12 db or a factor 16 for 0.50 cm signals).

The degree to which a medium absorbs radiation is usually denoted by an absorption coefficient γ (absorption per unit length) defined by $I=I_0\exp(-\gamma x)$, where I and I_0 are the intensities (energy/sec.) of a plane wave in the medium at x and at $x=0$, respectively. The absorption coefficient can also be expressed in decibels (db) per unit length defined by $A=(10/x)\log_{10}(I_0/I)=(4.343\cdots)\gamma$. In terms of the measured quantity, $\Delta e/e$, this latter absorption coefficient is[9]

$$A=-\frac{\lambda}{\lambda g}\frac{10}{6.19(10)^{-3}}\log_{10}\left(1-\frac{\Delta e}{e}\right)\text{ db/km}, \quad (1)$$

where λ and λg are, respectively, the free space wave-length and the wave-length in the wave guide absorption path.

[9] S. Ramo and J. R. Whinnery, reference 8, p. 345.

The quantity $\Delta e/e$ was measured relative to an evacuated wave guide path as a function of the pressure and composition of the absorbing gas and as a function of the signal frequency. The coefficient A was then calculated from changes in output meter readings. Several precautions and extraneous effects must be considered for this procedure.

EXPERIMENTAL PRECAUTIONS AND EXTRANEOUS EFFECTS

In order that $\Delta e/e$ be proportional to the absorption it is necessary that the detector-amplifier system be linear in the intensity of the incident wave. That is, one desires a pure square-law detector (detector voltage proportional to incident intensity) and a linear voltage amplifier. The amplifier linearity was checked with a calibrated 1000-cycle/sec. signal generator. The detector was checked by replacing the amplifier by a low impedance d.c. current meter and comparing the $\Delta e/e$ values given by the two methods. This is a useful procedure since it is well known that the short-circuit direct current from a crystal is more nearly linear with absorbed radio-frequency power than is the open-circuit voltage. At the signal levels used no non-linearities could be found.

When a gas is introduced into a wave guide, the ohmic losses in the wave guide change because of the change in dielectric constant ϵ of the medium. This is of interest since all gas losses were measured relative to an evacuated wave guide path. If α_{vac} and α_{gas} are the ohmic attenuations in db/meter, then

$$\alpha_{\text{gas}}\cong\alpha_{\text{vac}}(1+\Delta\beta),$$

where

$$\epsilon_{\text{gas}}=1+\Delta$$

and

$$\beta\cong\frac{\left(\frac{2a}{\lambda}\right)^2}{\left(\frac{2a}{\lambda}\right)^2+2\frac{b}{a}-1}-\frac{1}{2}\frac{\left(\frac{2a}{\lambda}\right)^2}{\left(\frac{2a}{\lambda}\right)^2-1},$$

a and b being, respectively, the wide and narrow dimensions of the wave guide.[10]

For the present wave guide path, this effect is less than 0.04 percent for all wave-lengths and

[10] S. Ramo and J. R. Whinnery, reference 8, p. 346.

gas pressures used and so is negligible as compared with noise fluctuations.

Another extraneous effect related to the dielectric constant of the gas is the change which it produces in the phase length between the source and detector. If standing waves exist in the wave guide path, a change in this phase length produces a change in the absorbed signal and hence in the detector output. If Γ_S and Γ_D are the amplitude reflection coefficients of the source and detector, respectively, then the maximum change possible in the absorbed power corresponds to $|\Delta e/e| = 8a^2\Gamma_S\Gamma_D$, where a is the reduction in amplitude which a wave suffers in one traversal of the path because of ohmic or other losses. For the apparatus used $a^2 \cong \frac{1}{16}$, so that for $\Gamma_S = \Gamma_D \leqslant 0.05$ the maximum $|\Delta e/e| \leqslant 0.12$ percent which is considered satisfactory in relation to the noise fluctuations. These very small reflection coefficients were attained with the double stub tuners shown in Fig. 1 and the absence of the above effect was checked by introducing lossless gases (argon or N_2) into the path. Of course, in order to carry $\Delta e/e$ from a maximum to a minimum, it is necessary to change the phase length of the path by $\lambda g/4$. This is about the phase change resulting when an atmospheric pressure of O_2 is introduced.

It might be thought that adsorbed vapors on the wave guide walls would produce losses which would change upon evacuation or that mechanical deformation of the wave guide with changing pressure would change the ohmic loss and so give rise to spurious effects. However, in the experiments with argon and N_2 no apparent absorptions were observed which could not be removed by eliminating standing waves in the path.

EXPERIMENTAL RESULTS AND CONCLUSIONS

The absorption was measured as a function of pressure for dried (P_2O_5) tank O_2 and for several O_2-N_2 mixtures at several wave-lengths in the $\frac{1}{2}$-cm range. A typical set of data are shown in Fig. 3.

It was found that the absorption per O_2 molecule was a function only of the wave-length and the *total pressure*. This indicates that O_2-O_2 and O_2-N_2 collisions are equally effective in determining the line breadth. However, the absorption per molecule at a given wave-length has a complex pressure dependence because of the large number of overlapping absorption lines, which are not resolved at atmospheric pressure.

In the center of the band (data at 0.48, 0.50

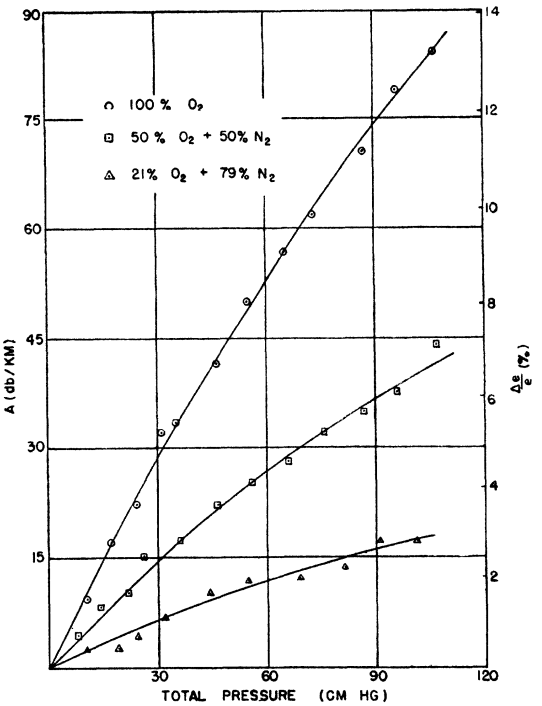

FIG. 3. Observed attenuation as a function of total gas pressure at $\lambda = 0.481 \pm 0.002$ cm and 22°C.

TABLE I. "Best fit" data at a total pressure of 76 cm Hg.

λ(cm)	Gas % by partial pressure	Temp. °C	A(db/km)	db/km in O_2	db/km in air
0.540±0.002	O_2	30	23.1	23.1	4.85
0.540±0.002	75% O_2+25% N_2	27	17.9	23.9	5.01
0.540±0.002	50% O_2+50% N_2	27	11.7	23.4	4.91
0.540±0.002	20% O_2+80% N_2	27	4.7	23.5	4.93
0.481±0.002	O_2	22	64.5	64.5	13.6
0.481±0.002	50% O_2+50% N_2	22	32.3	64.6	13.6
0.481±0.002	21% O_2+79% N_2	22	13.9	66.5	14.0
0.583±0.002	O_2	24	2.4	2.4	0.51
0.500+0.002	O_2	29	59.6	59.6	12.5
0.500+0.002	20% O_2+80% N_2	29	11.2	56.0	11.8
0.502±0.002	O_2	23	70.5	70.5	14.8
0.516±0.002	O_2	24	52.7	52.7	11.1
0.540±0.002	O_2	28	21.4	21.4	4.5
0.565±0.002	O_2	27	6.3	6.3	1.3
0.565±0.002	O_2	29	7.2	7.2	1.5
0.565±0.002	50% O_2+50% N_2	30	3.6	7.1	1.5
0.573±0.002	O_2	23	6.7	6.7	1.4
0.554±0.002	O_2	25	18.3	18.3	3.8
0.547±0.002	O_2	29	18.5	18.5	3.9
0.550±0.002	O_2	29	16.7	16.7	3.5
0.563±0.002	O_2	27	10.4	10.4	2.2
0.611±0.002	O_2	26	1.2	1.2	0.25

and 0.52 cm) the absorption per molecule decreases slightly with increasing pressure. At 0.54 cm the absorption per molecule is independent of the pressure. For longer wave-lengths the absorption per molecule increases with pressure, and finally approaches a linear pressure dependence in the far tails of the band (data at 0.56 cm and 0.58 cm).

The values of $\Delta e/e$ observed experimentally were reduced to db/km with Eq. (1) and plotted *vs.* total pressure as in Fig. 3 for each gas mixture and source wave-length. A smooth curve was then drawn so as to fit the plotted points. These "best fit" values of the absorption at a total pressure of 76 cm Hg are collected in the fourth column of Table I. In the fifth column these values are reduced to db/km in pure O_2 at 76 cm Hg and in the sixth column they are reduced to db/km in air (21 percent O_2) at 76 cm Hg, using the empirical result that the absorption coefficient is directly proportional to the O_2 partial pressure at constant total pressure.

The best fit values reduced to db/km in O_2 at 76 cm Hg are also shown in Fig. 4 together with Van Vleck's theoretical curves for a temperature of 27°C and several values of the line breadth parameter ($\Delta\nu/c$ in cm^{-1} for total pressure of 76 cm Hg). The best fit with these curves is seen to be in the range $0.02\ cm^{-1} < \Delta\nu/c < 0.05\ cm^{-1}$.

In assessing the agreement of the data with the theory it must be remembered that there are no adjustable constants except for $\Delta\nu/c$ and that in a large part of the experimental wave-length range the absorption is very insensitive to this.

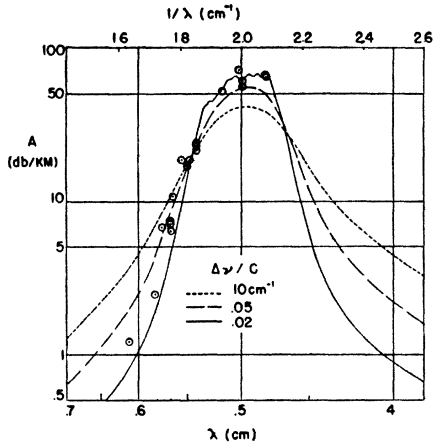

FIG. 4. "Best fit" data for pure O_2 and theoretical curves for pure O_2 at 76 cm Hg and 27°C.

Thus the agreement is in absolute terms and seems rather satisfactory.

On the other hand the accuracies of the data are not great enough to test the finer points of the theory: Whether $\Delta\nu/c$ is truly constant over the band, whether $\Delta\nu/c$ is accurately linear with total pressure, and the form and location of the individual absorption lines. Some of these points are of considerable interest and could be investigated with an improved apparatus, particularly with regard to higher intensity and greater frequency stability in the source and a more sensitive receiver. Then measurements could be made at low pressures and in the far tails of the band where these theoretical points are more easily investigated.