

THE ABSORPTION SPECTRUM OF OZONE IN SOLUTION

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[Handwritten signature]

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SUMMARY

The absorption coefficients of ozone in carbon tetrachloride and water were measured in the visible region of the spectrum. The absorption is composed of two singlet-triplet type transitions superimposed upon one another. The absorption contours of ozone in carbon tetrachloride were found to be equivalent to those of the gas, while the absorption coefficients were increased by a factor of five. An indication of the relaxation of the multiplicity rule, $M = 1 \leftrightarrow M = 3$ is suggested. The absorption contours of ozone in water were found to be quite different than those of the gas due to an increased intensity of one of the transitions with respect to the other. It is thought that the geometry of the molecule in the excited states is such that in the presence of a strong dipole, one transition becomes more probable than the other.

INTRODUCTION

In spite of extensive work on the spectrum of gaseous ozone in all wave length regions, the interpretation of even the coarser details of the spectrum in terms of the structure of the molecule remains somewhat obscure and is often in general disagreement among the different investigators.

The infrared region of the ozone spectrum has been studied in detail by a large number of investigators, ^(1,2,3,4,5,6) and yet there still exists a certain amount of ambiguity in the interpretation of the vibrational structure of the molecule. By use of the existing infrared data, varied sets of fundamental frequencies have been assigned to the molecule. The most generally accepted, although still imperfect interpretation is due to Penney and Sutherland ⁽⁷⁾ who attribute the 1043 cm^{-1} frequency to the ν_1 vibration, the 710 cm^{-1} frequency to the ν_2 vibration, and the 1740 cm^{-1} frequency to the ν_3 vibration.

The interpretation of the ultraviolet spectrum is also incomplete. Due to the complexity of the fine structure spectrum in this region, temperature sensitivity measurements made and interpreted by Eberhardt and Shand ⁽⁸⁾ do not define explicitly the three fundamental vibrational frequencies, but do indicate strongly the origin of the frequencies 1043 cm^{-1} and 710 cm^{-1} in complete agreement with Penney and Sutherland.

The Raman spectrum has been studied by Sutherland and Gerhard ⁽⁹⁾ and has been found to be non-existent within the long exposure times used. As the measurement is extremely difficult to perform, here again the data can not be considered conclusive.

Electron diffraction studies of the ozone molecule were conducted by Shand and Spurr⁽¹⁰⁾ where an obtuse angled model having O-O bond distances of 1.25 Å and 2.24 Å and a bond angle of 127° is suggested. The interpretation of the data has been modified recently by Eberhardt⁽¹¹⁾ to give a 100° model.

These structures are diametrically opposed, however, to that based upon infrared measurements which have been interpreted "unambiguously" recently by Adel and Dennison⁽¹²⁾ to indicate an acute angled model with a very strong O-O bond in the base and very weak bonding to the third O atom at the apex of the triangle, the O-O bond length at the base being 1.0 Å and the other O-O distances being such as to give an angle of 37° at the apex. In spite of this discrepancy, the obtuse angled model can be correlated more closely to the observed physical properties of the ozone molecule and is therefore generally considered correct.

The absorption in the visible region of the spectrum has been studied by a number of workers^(13,14,15) but even the experimental agreement is poor. Furthermore no adequate explanation of the origin of the visible spectrum has been offered.

PURPOSE OF THE INVESTIGATION

Since the decomposition rate of ozone in certain solutions is different from that in the gas, it was proposed that an investigation of the spectrum in solution might disclose certain facts related to the structure of the molecule and the spectrum in general as well as the decomposition mechanism. Thus in examining the spectrum we were chiefly concerned with (1) the general contours of the absorption in comparison to those of the gas, (2) the possible deviation of the spectrum from the Beer-Lambert law which would indicate association or other anomalies, (3) a quantitative comparison of the absorption coefficients in solution with those determined for the gas by other investigators, and (4) the comparison of coefficients and general absorption contours of the spectrum of ozone in different solvents.

To this end we have investigated the absorption in carbon tetrachloride in the region $3400 \text{ \AA} - 7000 \text{ \AA}$ and in water in the region $4500 \text{ \AA} - 6400 \text{ \AA}$. The investigations were both photographic and photometric. An ozonizer of novel design was constructed and utilized in the preparation of solutions. Both a large and small Bausch and Lomb quartz spectrograph of the Littrow type were used in the spectrographic experiments in the ultraviolet and visible regions, and a Beckmann quartz spectrophotometer with suitable modifications was used for obtaining more quantitative data on the absorption coefficients over the entire wave length region studied. A recording microphotometer was constructed for use in the interpretation of the photographic plates.

Using these two general techniques, we have been able to make some progress towards solving the problems proposed.

THE OZONIZER

Although constructed and operated along more or less generally known lines, a few distinguishing features of the ozonizer make it practical to discuss it briefly here.

In order to obtain ozone solutions of such a concentration that weak absorption regions may be measured accurately, it was necessary to build the ozonizer as carefully as possible keeping in mind that the percent conversion in electric discharge type ozonizers depends chiefly upon (1) the temperature of the oxygen in the electric discharge, (2) the potential difference across the ozonizer, (3) the character of the brush discharge produced, (4) the amount of negative catalysts, impurities or moisture within the ozonizer, and (5) the rate of flow of the oxygen through the apparatus.

A schematic diagram of the ozonizing apparatus is shown in Figure 1. A sulfuric acid drying tube, A, and two phosphorous pentoxide drying tubes, B and C, were used to remove any moisture entering the system with the tank oxygen. A dust filter, D, was incorporated into the ozonizer for the purpose of removing foreign matter which may have been picked up in the phosphorous pentoxide tubes. The removal of dust is absolutely necessary if a uniform brush discharge is expected. The ozonizer itself, E, consists of three concentric glass tubes carefully sealed together so that the walls of the ozonizing chamber are evenly spaced and are not more than two millimeters apart. A cooling solution is circulated through the outermost portion, the inner compartment being cooled in the same manner. For our purposes, it was found that tap water was sufficiently

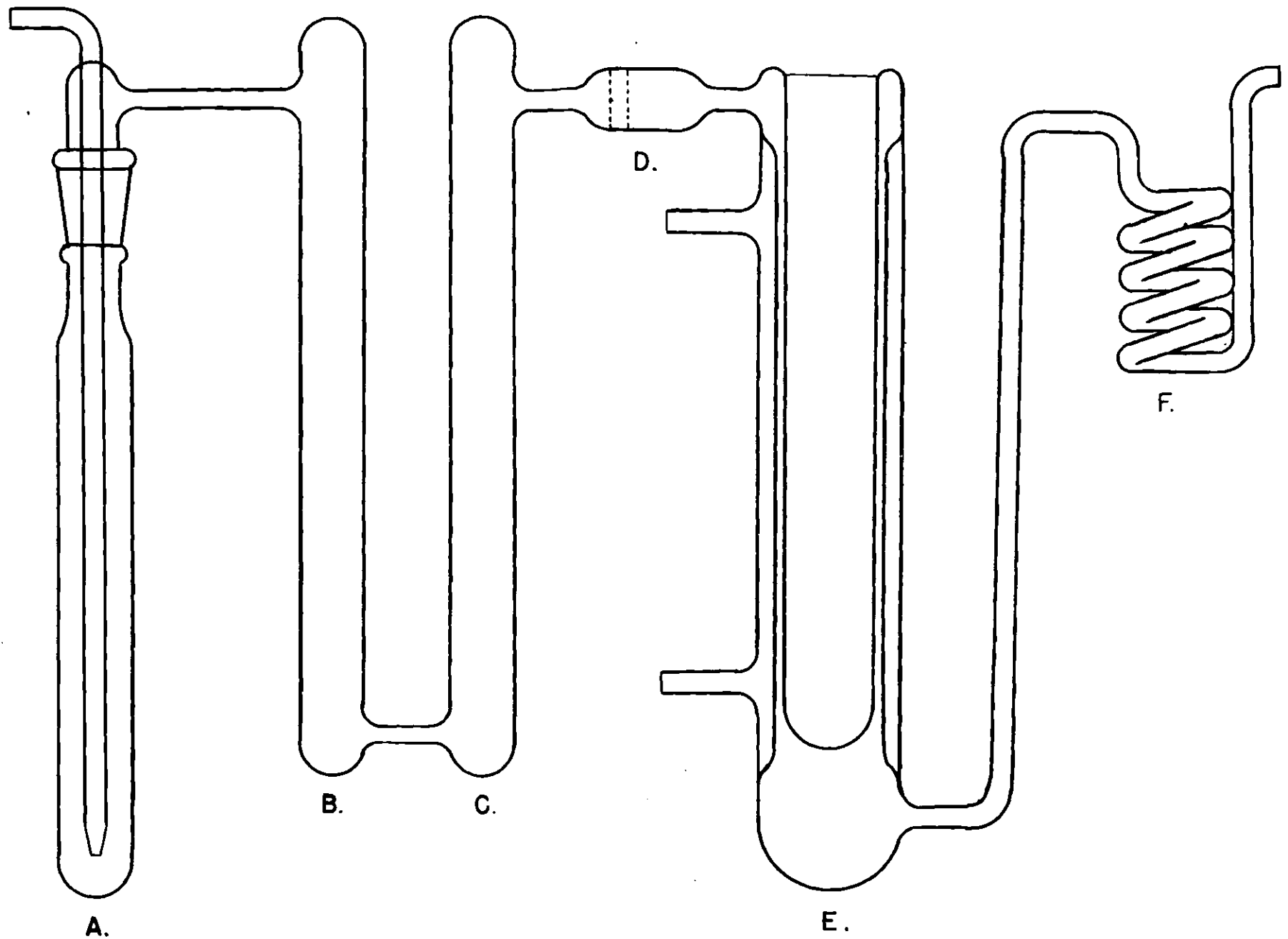
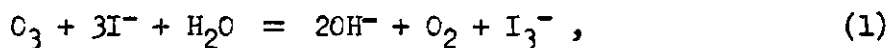


FIG. 1 OZONIZING APPARATUS

cool for this purpose and of great enough electrical conductivity that silvering of the apparatus was not necessary. If a higher conversion is desired, however, the ozonizer may be silvered and methyl alcohol at a very low temperature could be circulated through the cooling compartment. Actually, it was found that the percent conversion was only one to two percent higher at -60°C as compared to that at 20°C . The difficulties involved in attaining the lower temperature does not usually warrant its use. A potential difference of about 25,000 volts was applied across the ozonizing compartment by means of a 110,000 volt output x-ray transformer controlled by an auto-transformer operated on a 110 volt AC line.

After leaving the ozonizer, the ozone-oxygen mixture enters a cooling coil, F, which is immersed in a dry ice-methyl alcohol bath. The purpose of this coil is to remove any traces of nitrogen pentoxide which would interfere in the ozone spectrum. By extrapolating the data of Daniels and Bright⁽¹⁶⁾ to -78°C , the vapor pressure of nitrogen pentoxide was calculated to be 0.008 mm.

The percent conversion of the oxygen to ozone was determined by allowing the gas to bubble through distilled water until saturation was reached. A 0.2 molar potassium iodide solution buffered to 7 pH was added to a known amount of ozone solution, thus liberating free iodine by the reaction,



whose concentration was determined colorimetrically against prepared standards in the Beckmann spectrophotometer. Assuming Henry's law and using

0.514 for the Bunsen coefficient at 1°C as interpolated from the data of Briner and Perrottet,⁽¹⁷⁾ the percent ozone in the gaseous mixture was calculated. The ozonizer cooled with tap water to about 20°C was found to yield a gaseous mixture containing about 7% ozone by volume, i.e., 10% by weight.

THE ABSORPTION SPECTRUM OF OZONE IN CARBON TETRACHLORIDE

As ozone is quite soluble in carbon tetrachloride, an extensive amount of work was done upon the absorption spectrum of the gas in this solvent.

The carbon tetrachloride was purified in the following manner. U.S.P. grade solvent was first treated with concentrated sulfuric acid, then refluxed for about an hour to remove any phosgene which may have been formed. The carbon tetrachloride was then distilled slowly, the first and last 10% being discarded. The distillate was saturated with ozone and allowed to stand about twenty-four hours in order to remove any impurities not removed by the sulfuric acid, refluxed again and distilled from phosphorous pentoxide. The carbon tetrachloride obtained was pure enough to inhibit any rapid formation of scattering material during absorption measurements. The ozone solution, however, will become slightly cloudy over a period of twenty-four hours due to reaction of ozone with the carbon tetrachloride.

1. Spectroscopic Investigation.

It seemed necessary to make a rough qualitative measurement of the absorption contours of ozone in carbon tetrachloride in order to compare them with those of the gas and to obtain an insight on what might be expected in our quantitative work. These measurements were made spectrographically.

A saturated solution of ozone in purified carbon tetrachloride was placed in a glass absorption cell 60 centimeters in length constructed from one-inch pyrex tubing on whose ends photographic cover glasses were sealed by means of fused silver chloride. The light source was a 500 watt projection bulb.

A series of photographs in the region $3800 \text{ \AA} - 6200 \text{ \AA}$ were made on a large Bausch and Lomb Littrow type quartz spectrograph using Eastman type 103F plates at various exposure times. As we were interested only in the qualitative aspects of the absorption, no attempt was made to account for variations of light source intensity with wave length or absorption due to the glass or carbon tetrachloride. A simple recording microphotometer was constructed for use in determining the resulting absorption contours. The plates were calibrated by means of a calibration curve derived from an iron arc spectrum on each plate. Figure 2 shows the absorption contours of the ozone in carbon tetrachloride spectrum in the visible region as obtained spectrographically.

It was found that the resulting spectrum of the ozone solution closely resembles that of gaseous ozone as determined by Vassey.⁽¹⁸⁾ No fine structure was discovered as reported by Colange.⁽¹⁹⁾

TABLE I

ABSORPTION MAXIMA OF OZONE IN THE GAS AND IN SOLUTION

GAS		SOLUTION
<u>Vassey</u>	<u>Colange</u>	<u>Our Work</u>
4808 \AA	4810 \AA	4839 \AA
5056 \AA	5042 \AA	5050 \AA
	5345 \AA	5355 \AA
5754 \AA	5750 \AA	5721 \AA
6010 \AA	6067 \AA	6009 \AA

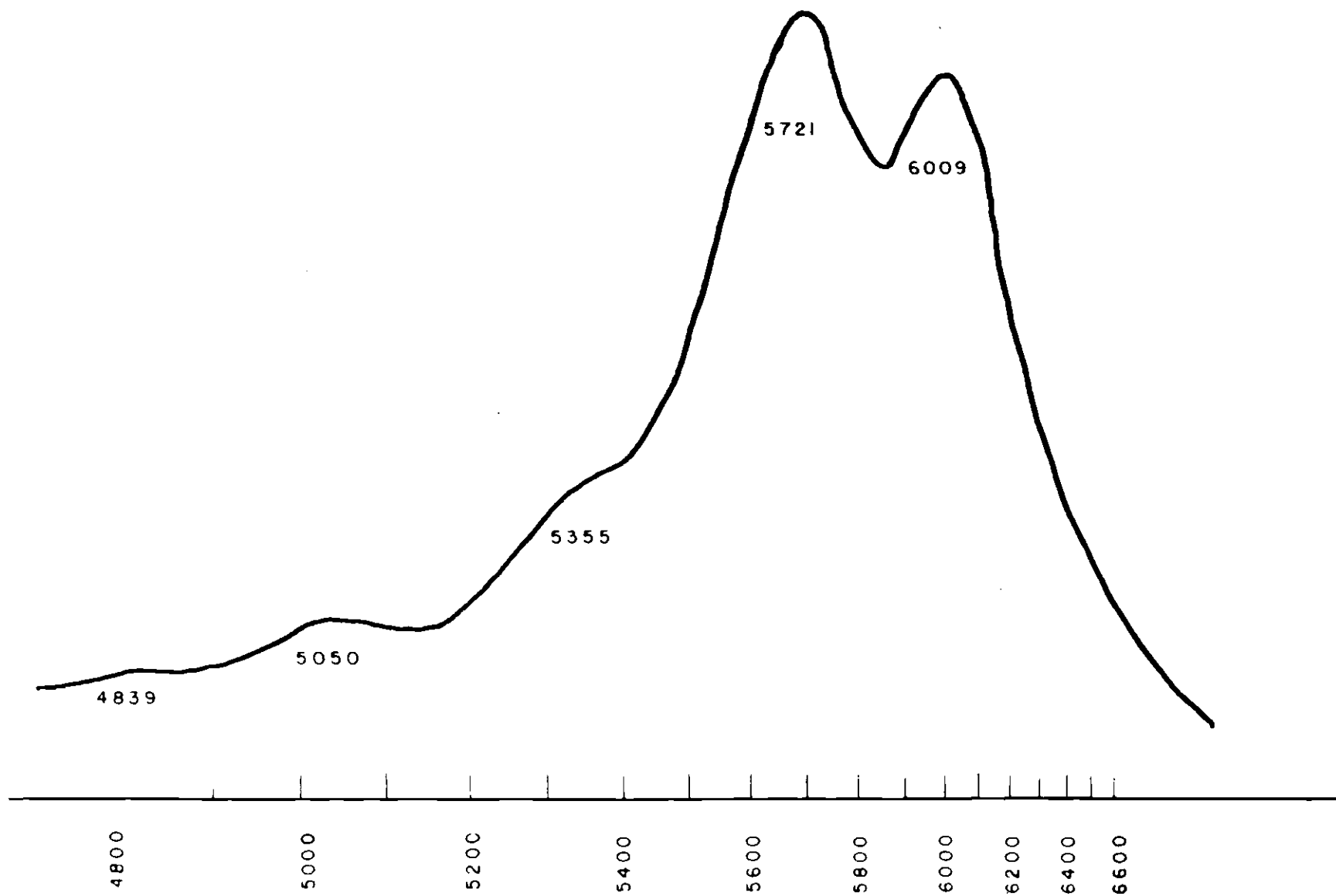


FIG. 2 ABSORPTION CONTOURS OF OZONE IN CARBON TETRACHLORIDE
AS OBTAINED SPECTROGRAPHICALLY

Table I gives a correlation between the values of wave length for maximum absorption of ozone in the gas and in solution. A great number of lesser absorption maxima were reported by Colange but are omitted from the table.

Although there is a very slight variation in slope of Vassey's curve at about 5350 \AA , there is no other indication that a maximum exists at this point. In our work, however, this maximum showed up consistently throughout the measurements. Due to the qualitative aspects of the work at this point, it was impossible to verify the existence of this peak which may indeed have arisen from a rather large light source intensity in this region.* In general, however, the contours of absorption are very similar, if not identical, to those of the gaseous spectrum. The fine structure reported by Colange probably does not exist in the gas and most certainly not in solution due to the "washing-out effect" caused by pressure broadening of the lines. Recent observations have shown that no fine structure exists in the gaseous spectrum of ozone at atmospheric pressure.⁽²⁰⁾ It will be interesting to see the results of some yet unpublished work by F. S. Wilson⁽²¹⁾ where the visible absorption spectrum of gaseous ozone at pressures as low as a few millimeters has been measured.

2. Spectrometric Measurements.

The absorption coefficients of ozone in carbon tetrachloride in the range $3400 \text{ \AA} - 7000 \text{ \AA}$ were determined accurately by use of a

*The absorption maximum at 5355 \AA will be verified later by more precise measurements.

modified Beckmann DU model quartz spectrophotometer. The accuracy of the instrument was found to fall off rapidly at the higher wave lengths due primarily to scattered visible light within the instrument finding its way through the exit slit.

Special efforts were made to obtain a non-varying light source, a constant temperature, and a well mixed ozone solution at all times. Results in the optimum operating range of the spectrum were quite reproducible to one percent.

The spectrophotometer was set up as shown in Figure 3 such that a 60 centimeter pyrex absorption cell could be placed between the light source and the photometer entrance slit. This was done by removing the cell holder and lamp housing from the instrument, directing the end of the absorption cell into the slit opening of the photometer and placing a 100 watt projection bulb at the far end of the cell. The absorption cell is similar to that used in the spectrographic determination except that provisions were made for mixing and diluting the solution within the cell, and the cell ends were constructed from 1 millimeter polished pyrex glass plates trimmed to size and fused directly to the pyrex tube. This latter change was necessary in order to prevent constant cell fracture which occurred when the silver chloride ends were used. It was found necessary to immerse the cell permanently in a thermostat controlled constant temperature bath so that temperatures could be controlled within 0.05°C . This precaution was mandatory not so much due to the fact that absorption coefficients and contours may change with temperature, but that the light path through the tube and therefore its intensity at the entrance slit was found to be very sensitive to temperature changes as small as 0.5°C .

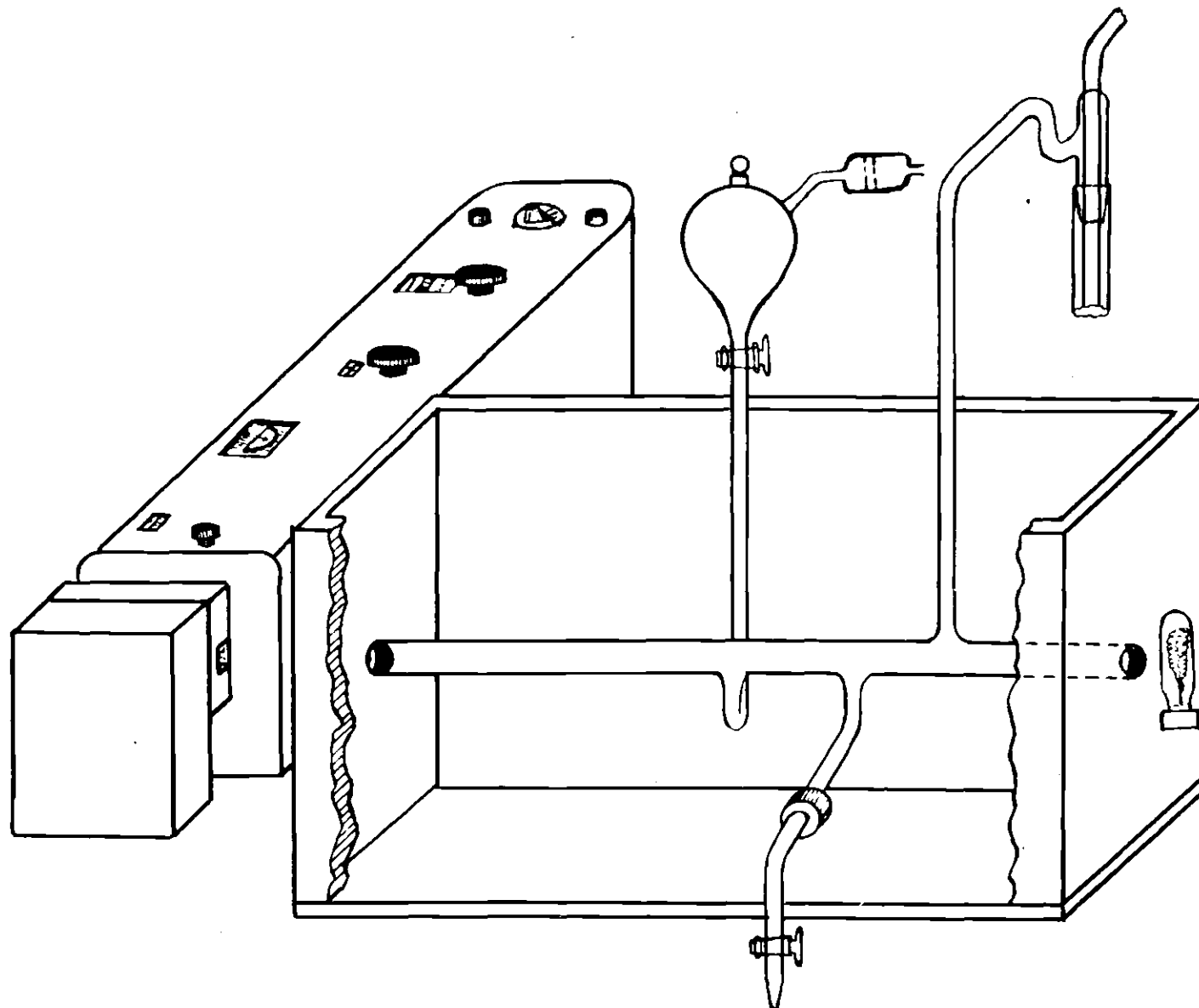


FIG. 3 ARRANGEMENT OF APPARATUS FOR THE SPECTROMETRIC MEASUREMENT OF ABSORPTION COEFFICIENTS OF OZONE IN SOLUTION

It was decided that this marked effect was due primarily to changes in refractive index of the glass and changes in the contours of the reflecting walls of the tube. We were also unable to use any lenses or filters adjacent to the light source as the same difficulties were involved. The 100 watt projection bulb alone was of great enough light intensity that exact measurements could be made with narrow slit widths, and the heat intensity was low enough so that it could be controlled easily with a forced draft.

The absorption cell was provided with a number of special provisions for the purpose of mixing and diluting the ozone solutions without disturbing the cell, as well as a side arm for obtaining samples. It was discovered that samples could not be taken from the cell by means of a pipette since the reduced pressure above the solution would tend to remove much of the ozone thus causing large errors in the analyses. Samples were run directly into a 25 cc volumetric flask into which a known amount of buffered 7pH potassium iodide had been placed. The loss of ozone by diffusion to the atmosphere was negligible.

The ozonizing apparatus was connected directly to the absorption cell so that there was no chance for any contaminants from the air to enter the apparatus during mixing. A one liter separatory funnel connected upright to the cell by a standard taper joint served as a reservoir in which the ozone solutions were prepared, diluted and mixed. Various dilutions were made by merely shutting off the electrical discharge in the ozonizer and bubbling the dry, dust-free oxygen through the solution. A removable dry-ice trap was incorporated into the apparatus so that no carbon tetrachloride vapor could back up into the ozonizer.

The absorption coefficients were determined in the following manner. From the Beer-Lambert law we know that the transmission of light, T , is equal to:

$$I/I_0 \equiv T = 10^{-\alpha pl}, \quad (2)$$

where:

- I_0 = the light intensity traversing solvent only;
- I = the light intensity traversing ozone in solvent;
- α = absorption coefficient;
- p = concentration of ozone in solution;
- l = light path length in centimeters.

From equation (2),

$$-\log I = \alpha pl + K \equiv D, \quad (3)$$

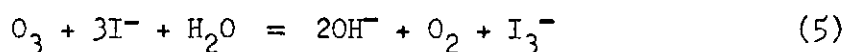
where D is the optical density, and K is a constant depending upon I_0 , we have

$$dD/dp = \alpha l. \quad (4)$$

If Beer's law is followed, and I_0 is kept constant during a determination, D plotted against the concentration should give a straight line whose slope is related to the absorption coefficient by equation (4).

Figure 4 shows a plot of D vs. p at the wave length 6050 Å.

The concentration of ozone was determined by an iodometric titration making use of:



at pH = 7.

The liberated iodine from 10 cc ozone sample was titrated with freshly standardized 0.001N $Na_2S_2O_3$ in solution slightly acid with acetic

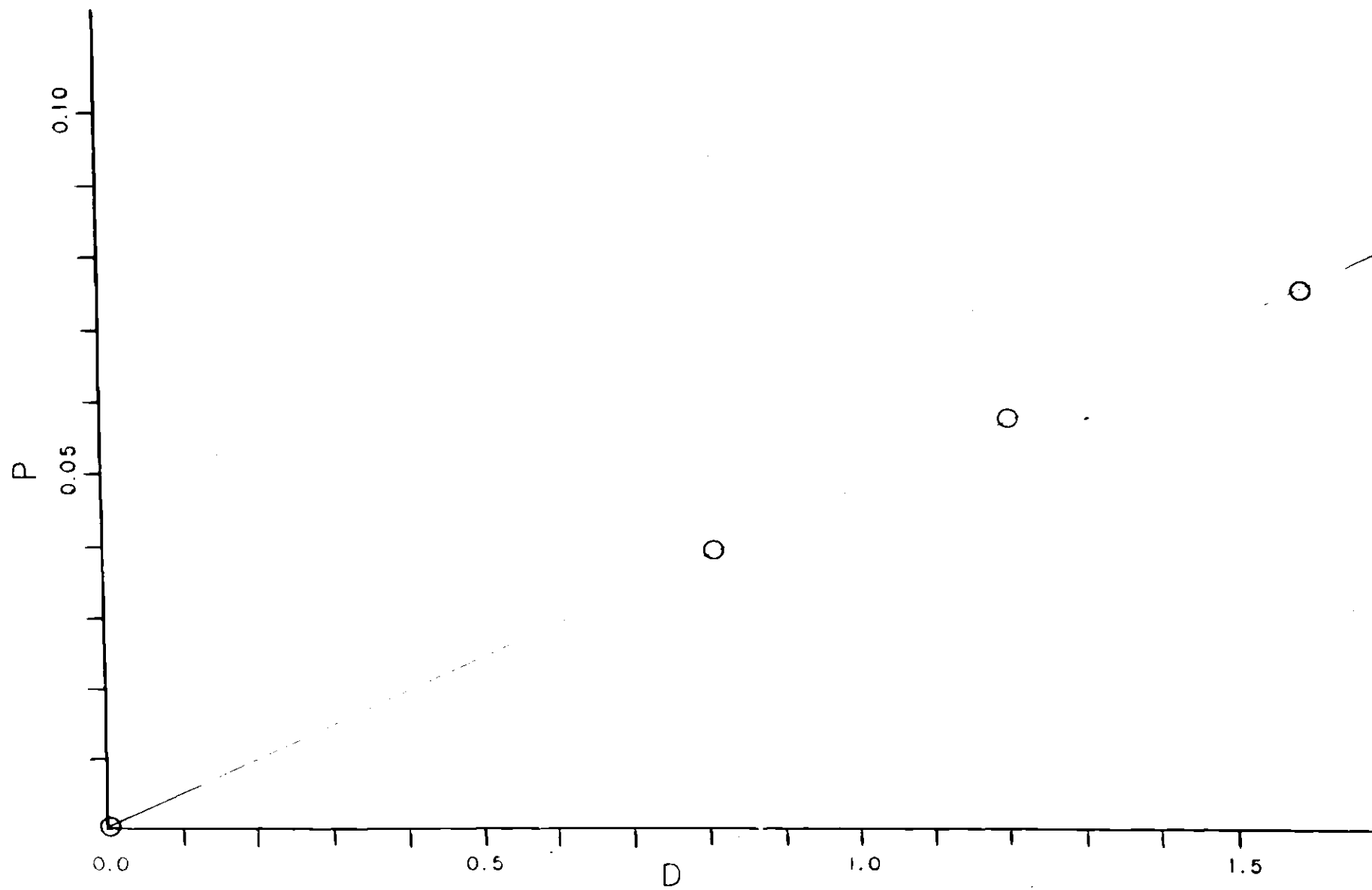


FIG. 4 OPTICAL DENSITY OF OZONE IN CARBON TETRACHLORIDE
PLOTTED AGAINST CONCENTRATION IN ATMOSPHERES FOR 6050 Å

acid. Starch was used as the indicator. It was found necessary to make the titrations in an atmosphere of nitrogen since the concentrations are of such small magnitude that oxidation of the acidified KI by atmospheric oxygen causes appreciable error. The concentration of ozone in moles per liter of solution was converted into atmospheres in order to facilitate the comparison with data on the gas.

The light path length through the absorption cell was measured by use of various dilutions of a 0.01 molar solution of potassium permanganate whose absorption coefficient was measured in the spectrophotometer. This substance was found to follow Beer's law for large differences in concentration. The light path length was found to equal the cell length.

The absorption coefficients at 5000 \AA and 6050 \AA were determined accurately by the above method. Absorption coefficients at intermediate wave lengths were found by use of the following relationship, derived by equating \underline{pl} in equation (3) for two different wave lengths, \underline{x} and \underline{s} . We obtain on differentiating,

$$\alpha_x = \alpha_s \frac{dD_x/dD_s}{dD_s/dD_s} . \quad (6)$$

By plotting the optical density at the unknown wave length against the optical density at any of the standard wave lengths for a number of arbitrary but not necessarily known concentrations, one may obtain the absorption coefficient at the unknown wave length. It is absolutely necessary, of course, to record the data as rapidly as possible so that the concentration of the ozone solution will not change during a given measurement. The rate of decomposition of ozone in carbon tetrachloride is slow enough so that measurements may be carried on for several different wave

lengths at a time without the fear of error. A typical example of the determination of absorption coefficients for wave lengths in the vicinity of 6000 \AA is given below. The data for such a measurement are listed in Table II and the plot D_x vs. D_{6050} is given in Figure 5.

TABLE II
TYPICAL OUTLINE OF DATA OBTAINED
FOR DETERMINATION OF ABSORPTION COEFFICIENTS

DILUTION NO.	$t = 30.0^\circ\text{C}$				
	D_{6050}	D_{6250}	D_{6100}	D_{5800}	D_{5700}
1.	1.744	1.743	1.762	1.312	1.264
2.	1.439	1.503	1.458	1.030	0.983
3.	1.279	1.387	1.339	0.893	0.848
4.	1.177	1.293	1.218	0.775	0.732
5.	1.014	1.165	1.068	0.627	0.583
6.	0.711	0.942	0.790	0.355	0.313

The absorption coefficients for ozone in carbon tetrachloride for wave lengths between 3400 \AA and 6900 \AA are listed in Table III. As many

*** A study of slit width effects upon absorption measurements was made by W. H. Eberhardt and the author. It was found that a slit width x nominal band width factor greater than about 10 millimicrons would be sufficient to cause an apparent deviation from Beer's law in the optical density vs. concentration curves. It is also well known that excessive slit widths tend to "blur" the spectrum whereby fine structure may be lost.

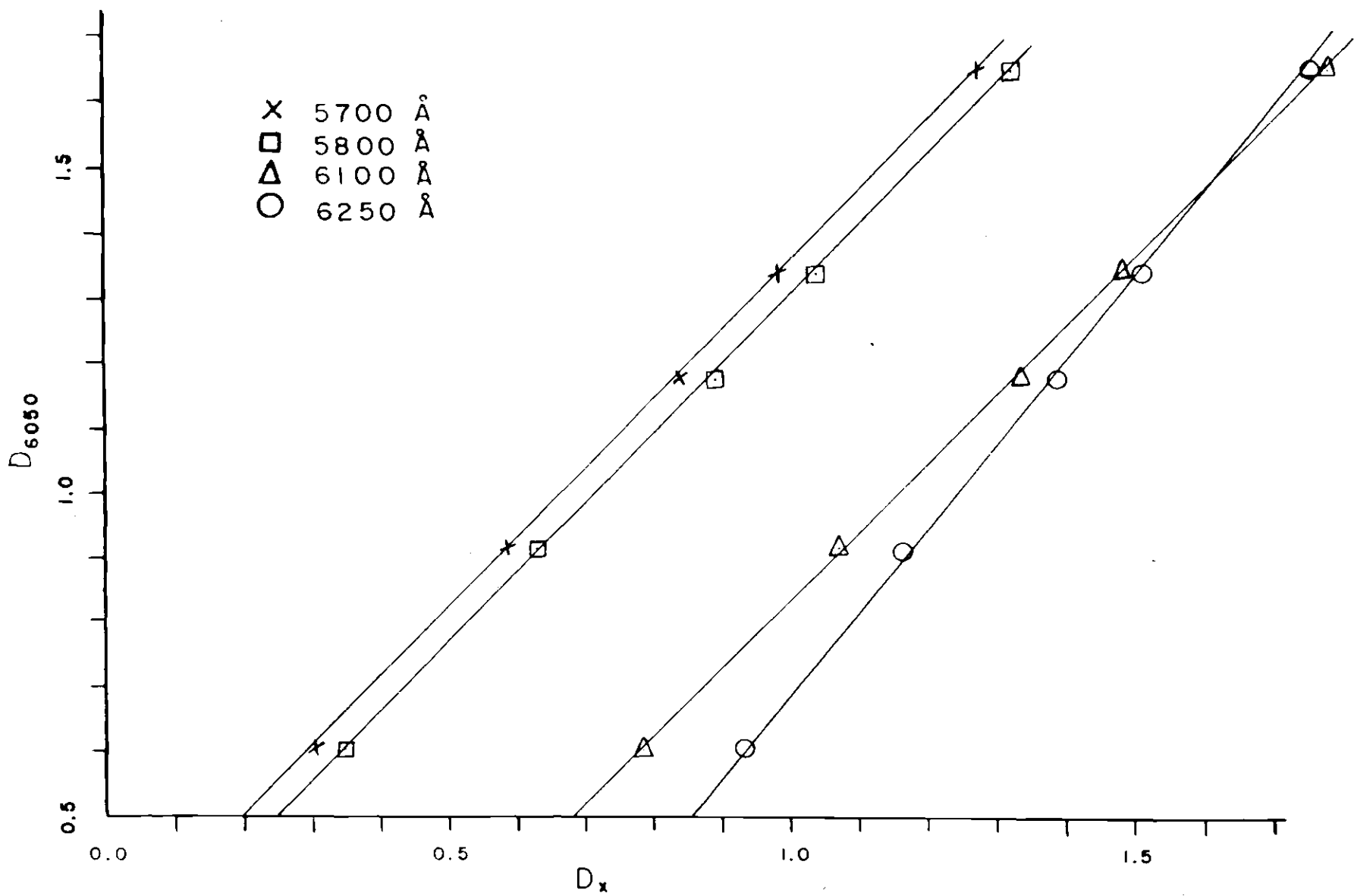


FIG. 5 PLOT OF OPTICAL DENSITY AT 6050 Å vs OPTICAL DENSITY AT SOME OTHER WAVE LENGTHS FOR OZONE IN CARBON TETRACHLORIDE

TABLE III
 ABSORPTION COEFFICIENTS OF OZONE IN CARBON TETRACHLORIDE

Wave Length	Absorption Coefficient,	Wave Length	Absorption Coefficient,
3400 Å	0.062	5500 Å	0.245
3500 Å	0.039	5550 Å	0.264
3600 Å	0.019	5600 Å	0.286
3700 Å	0.012	5650 Å	0.311
3800 Å	0.007	5700 Å	0.327
3900 Å	0.005	5720 Å	0.331
4000 Å	0.003	5740 Å	0.332
4100 Å	0.003	5750 Å	0.333
4200 Å	0.004	5800 Å	0.330
4300 Å	0.005	5850 Å	0.331
4400 Å	0.007	5900 Å	0.345
4500 Å	0.009	5950 Å	0.356
4600 Å	0.014	6000 Å	0.360
4700 Å	0.027	6050 Å	0.350
4740 Å	0.036	6100 Å	0.335
4800 Å	0.043	6150 Å	0.315
4840 Å	0.048	6200 Å	0.295
4900 Å	0.057	6250 Å	0.273
5000 Å	0.087	6300 Å	0.255
5050 Å	0.101	6400 Å	0.223
5100 Å	0.107	6500 Å	0.191
5200 Å	0.132	6600 Å	0.164
5300 Å	0.190	6700 Å	0.140
5350 Å	0.198	6750 Å	0.128
5400 Å	0.211	6800 Å	0.117
5450 Å	0.228	6900 Å	0.097

as five measurements were sometimes necessary at a single wave length. Values given in Table III are weighted and averaged and do not necessarily correspond to any single measurement. Comparative curves of absorption coefficients vs. wave length for ozone in carbon tetrachloride and ozone gas are shown in Figure 6. It will be noticed that absorption coefficients of the ozone in solution are from five to six times greater than those in the gas while the contour of absorption in this region is essentially identical.

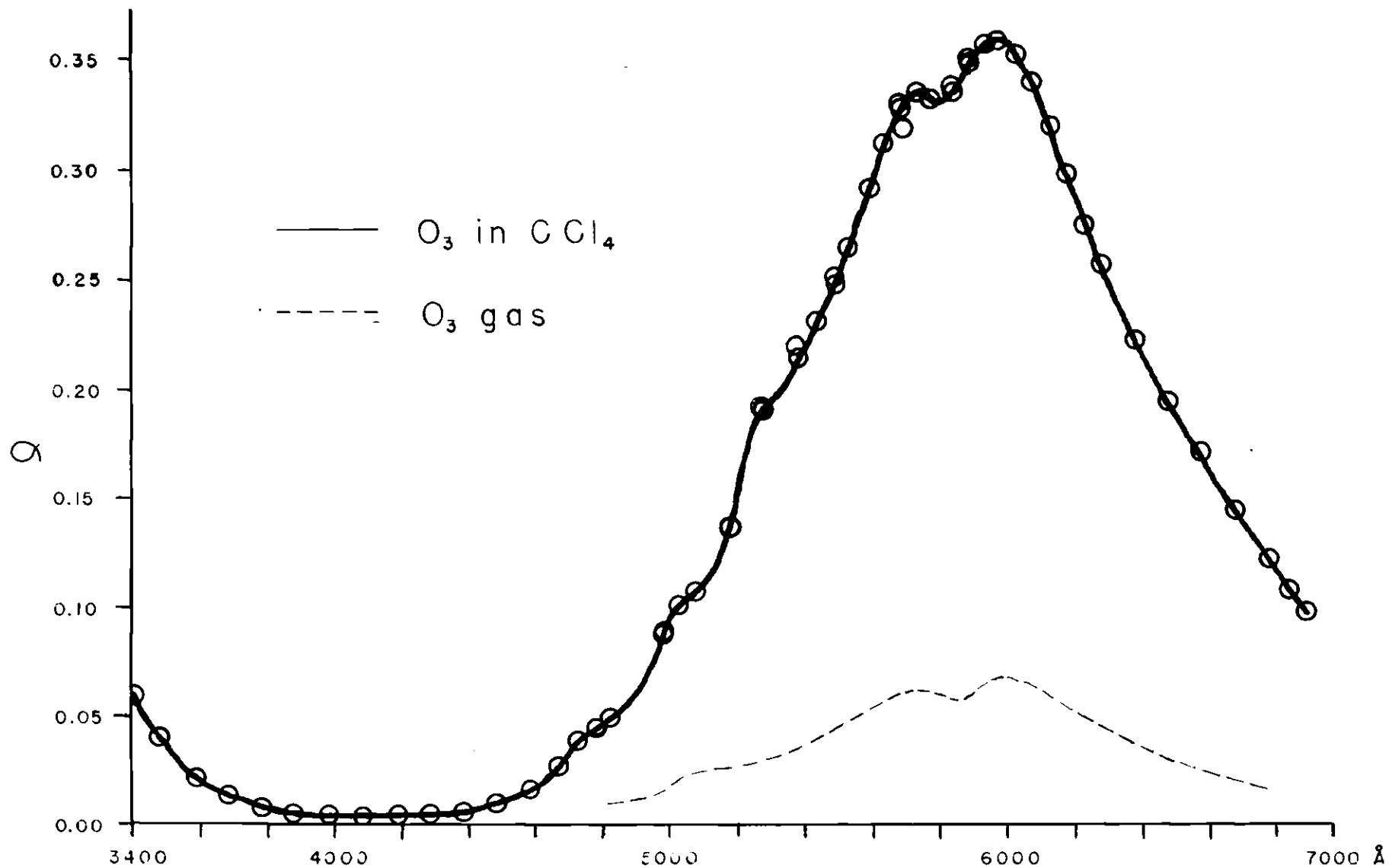


FIG. 6 ABSORPTION COEFFICIENTS OF OZONE IN CARBON TETRACHLORIDE AND IN THE GAS vs WAVE LENGTH

THE ABSORPTION SPECTRUM OF OZONE IN WATER

Water was chosen as the other solvent in which the ozone spectrum was studied. The choice was made in contrast to carbon tetrachloride in view of the large dipole moment of the water molecule, its low index of refraction, its small size, and the rather rapid decomposition rate of ozone in water. Actually it was found that this selection left much to be desired, for the measurements of absorption coefficients were extremely difficult to make. Ozone is far less soluble in water than it is in carbon tetrachloride and, as will be seen, the absorption coefficients are smaller. The difference in optical density between pure water and a concentrated solution of ozone in water is so extremely small for all spectral regions that only approximate values for absorption coefficients could be obtained. In order to facilitate the making of measurements, a 0.001N H_2SO_4 solution was used as a solvent. It was found that the spectrum remained essentially unchanged within experimental error while the decomposition rate of the ozone decreased considerably in the acid solution.

The absorption coefficients were measured in the same manner as before. Titration measurements were made at wave length 6050 Å, the absorption coefficients at other wave lengths being determined by graphical comparison of optical densities at several arbitrary concentrations. The measurements were repeated several times in order to obtain a good average value of absorption coefficient. The results obtained in this manner were usually reproducible to within 10%. A list of absorption coefficients for ozone in water solution in the region 4300 Å - 6300 Å is given in Table IV. The plot of absorption coefficients vs. wave length for ozone in water

TABLE IV
 ABSORPTION COEFFICIENTS OF OZONE IN WATER

Wave Length	Absorption Coefficient,
4300 Å	0.004
4500 Å	0.012
4600 Å	0.017
4700 Å	0.027
4800 Å	0.046
4900 Å	0.064
5000 Å	0.089
5100 Å	0.115
5200 Å	0.130
5300 Å	0.150
5400 Å	0.173
5500 Å	0.190
5600 Å	0.205
5700 Å	0.216
5800 Å	0.216
5900 Å	0.210
6000 Å	0.202
6050 Å	0.200
6100 Å	0.196
6200 Å	0.178
6300 Å	0.144

solution as compared to gaseous ozone is shown in Figure 7. Perhaps the most striking feature of the results lies in the fact that the absorption maximum at 6009 Å has been almost entirely suppressed or shifted while the absorption at 5721 Å is of approximately the same magnitude and shape as that of ozone in carbon tetrachloride. Compare with Figure 6.

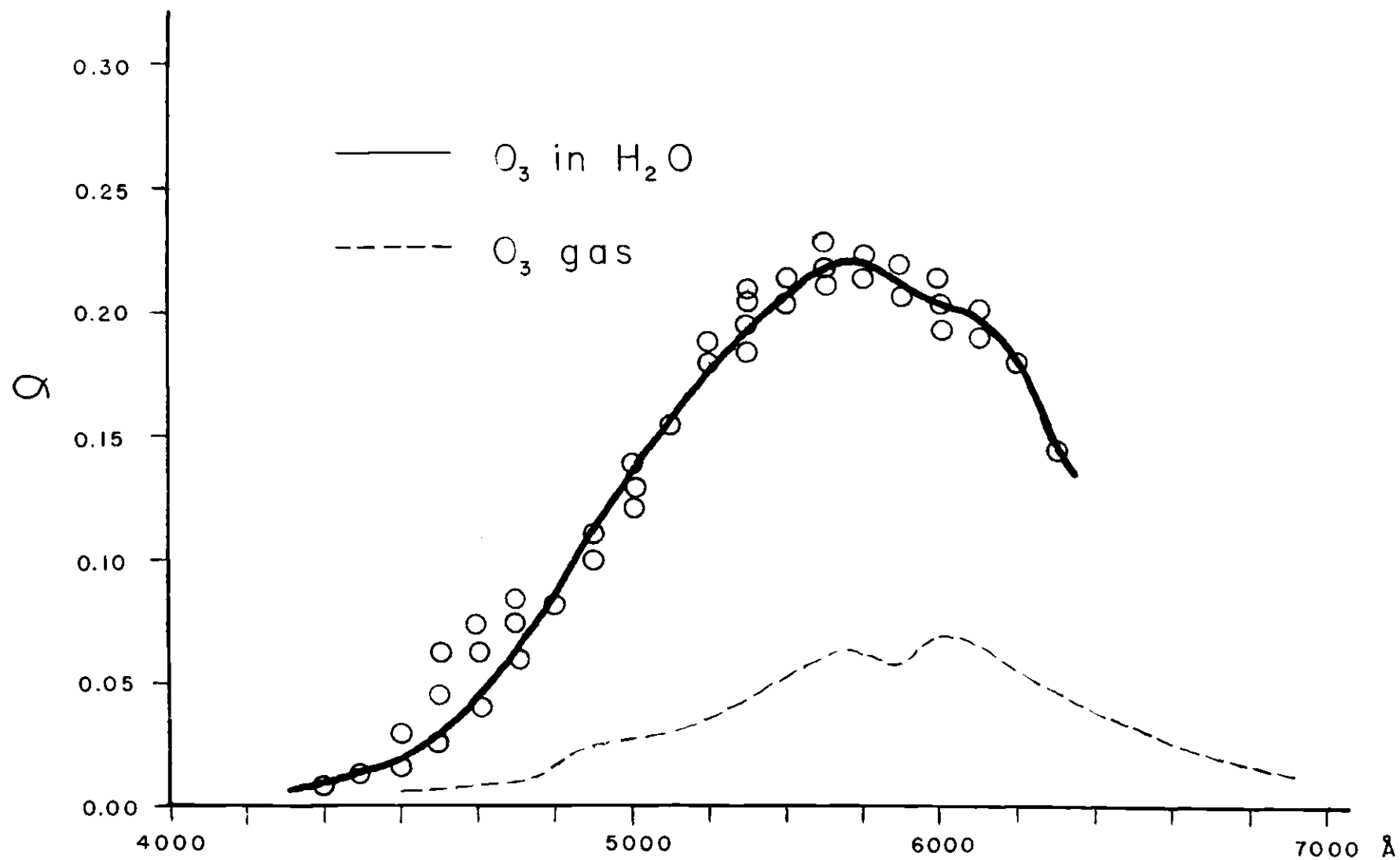


FIG. 7 ABSORPTION COEFFICIENTS OF OZONE IN WATER AND THE GAS vs WAVE LENGTH

DISCUSSION OF DATA

The comparative absorption coefficients of gaseous ozone and of ozone in solutions of carbon tetrachloride and water plotted against wave number are shown in Figure 8. The two most striking features of the results, namely the increased absorption coefficients of ozone in solution and the absorption contour differences in the water, will be discussed separately.

The heats of solution of ozone in water and carbon tetrachloride have been measured by Briner and Perrottet⁽²²⁾ and are given as 3.9 kcal/mol and 5.9 kcal/mol, respectively. The comparatively large heat of solution of ozone in carbon tetrachloride would suggest immediately that a fairly strong interaction exists between the ozone molecule and the carbon tetrachloride molecule. This fact is further substantiated in view of the great solubility of ozone in this solvent.*** The interaction is believed to be a dipole-induced dipole type resulting from the quite large polarizability of the carbon tetrachloride molecule. According to the absorption contours of the spectrum, however, it is obvious that since no frequency shift in the maxima exists, there can be no structural change in the ozone molecule unless it takes place in the ground and excited states alike. A change in structure of either ground or excited states independently would give rise to different energy values for the transitions and thus cause a shift in the maxima.

It would be expected that the large dipole moment of the water

*** 4.6 cc of ozone at S.T.P./cc CCl_4 at $t = -12^\circ\text{C}$ (23)
2.8 cc of ozone at S.T.P./cc CCl_4 at $t = 0^\circ\text{C}$

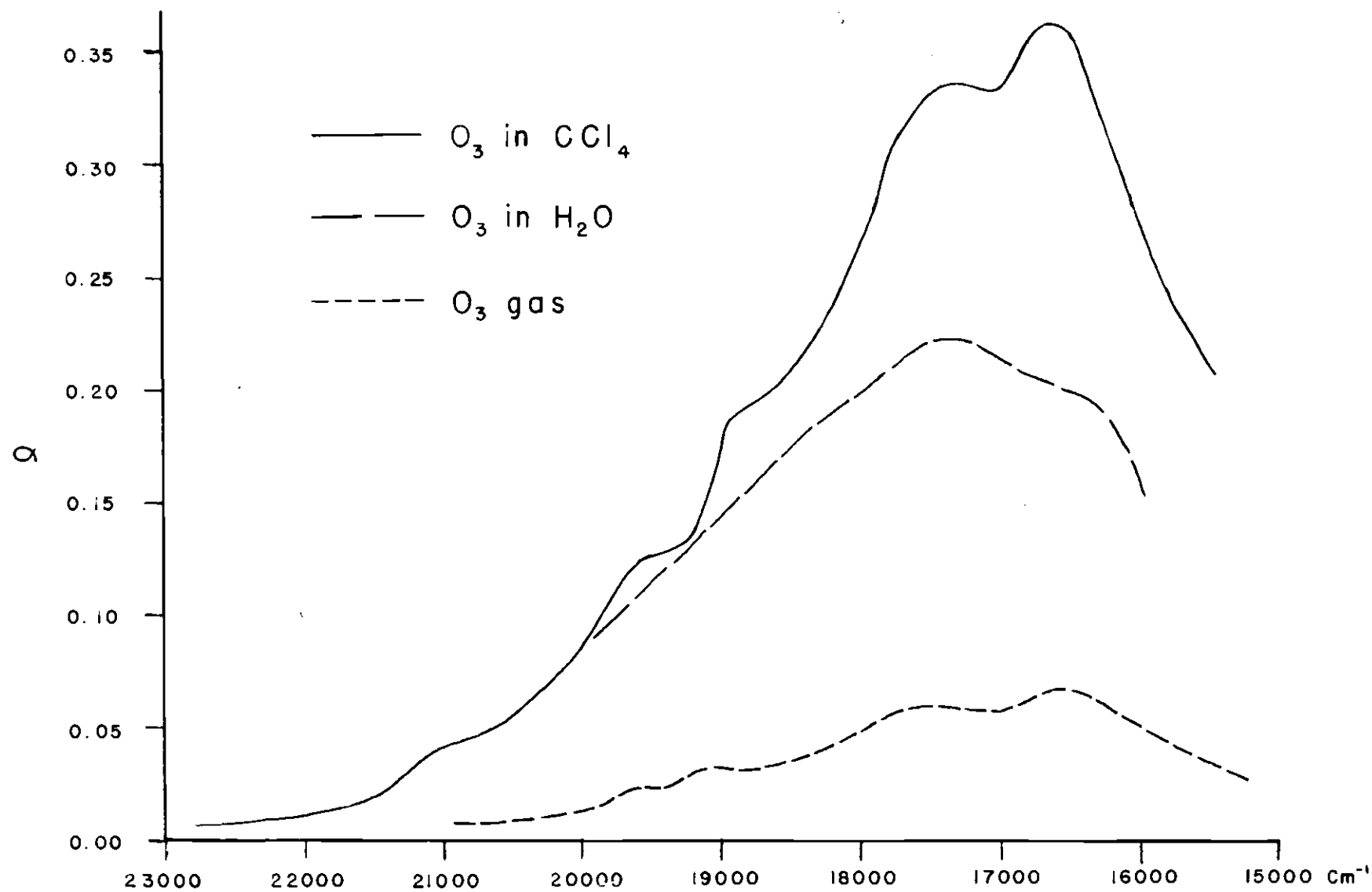


FIG. 8 ABSORPTION COEFFICIENTS OF OZONE IN CARBON TETRACHLORIDE, WATER AND THE GAS vs WAVE NUMBER

molecule would set up an even stronger dipole-dipole interaction between ozone and water, contributing to a heat of solution and solubility larger than those observed. It is possible that so strong a mutual interaction exists between water molecules that the ozone-water interaction is greatly retarded, or that the ozone molecule in water solution is distorted in some fashion by the action of the water molecules. A distortion of the ozone molecule in water solution would cause a change in the shape or position of the potential functions, which may give rise to a shift towards the blue. As the bond lengths of the excited states are longer than those of the ground state, it would be expected that a dipole or induced dipole interaction would tend to weaken the bonds of the excited states to a greater extent than those of the ground state. A shift of the maximum would then result. It does not seem plausible, however, that the water interaction could be stronger than that of carbon tetrachloride in view of the great solubility of ozone in the latter. No great shift of the maxima should then be expected in water. It is well worth noting recent measurements by F. S. Wilson⁽²⁴⁾ upon gaseous ozone contaminated with water vapor indicate a retardation rather than a shift of the 6009 Å⁰ maximum.

To summarize then, a rather strong dipole-induced dipole interaction takes place between the carbon tetrachloride and ozone. This interaction does not alter the structure of the ozone molecule in the ground or excited states independently. The dipole-dipole interaction of ozone and water, if existent, is rather weak due probably to the strong mutual interaction of water molecules which tends to "squeeze" the ozone out of solution. If a change in structure of the ozone molecule occurs in water solution, it must take place to an equal extent in the ground and excited states, for no shift of the absorption maxima is observed. A suppression

of the 6009 Å maximum is indicated in respect to the 5721 Å maximum.

These considerations suggest that two different type transitions are superimposed upon one another, one whose transition probability with respect to that of the other is enhanced to a greater extent by the surrounding electric dipole of the water.

If it is assumed that the dissociation products of an ozone molecule are one molecule of oxygen and one atom of oxygen in their various known electronic states, one may deduce the symmetry properties and multiplicities of the excited states of ozone. See Table V below.

The location and intensity expected for many of the allowed transitions computed in this way are in accord with observed transitions in the ultraviolet. It will be noticed that a singlet-triplet type transition, forbidden by the multiplicity rule $M = 1 \leftrightarrow M = 3$, with a dissociation limit at 6200 Å is also postulated by this scheme. It necessarily would be expected that this transition be weak as compared to any of the allowed transitions which comprise the ultraviolet. As the two maxima of ozone occur in the neighborhood of 6200 Å and their absorption coefficients in the gaseous spectrum are of an order of 1/2500 as great as that of the allowed transition at 2550 Å, it is not unreasonable to assume that the 5721 Å transition and the 6009 Å transition are also of a singlet-triplet type, differing only in geometry or symmetry properties in the excited states.

Effects similar to these have been observed in the case of bromine in solution⁽²⁵⁾ where the two transitions occurring at 4150 Å and 4950 Å are influenced to a different degree by various type solvents. Bromine in water solution exhibits only one broad maximum at 3900 Å, the 4950 Å

TABLE V

SYMMETRY PROPERTIES AND MULTIPLICITIES OF THE EXCITED STATES OF OZONE****

DISSOCIATION PRODUCT	ΔE	MOLECULAR STATES		
		Symmetry	Multiplicity	λ
$^3\Sigma^+ 3p$	1.05	A_1	5, 3, 1	12,000 $\overset{\circ}{\text{A}}$
$^1\Delta^+ 3p$	2.0	A_1, A_2, B_1	3	6200 $\overset{\circ}{\text{A}}$
$^1\Sigma^+ 3p$	2.67	A_1	3	4650 $\overset{\circ}{\text{A}}$
$^3\Sigma^+ 1d$	3.0	A_1	3	4140 $\overset{\circ}{\text{A}}$
$^1\Delta^+ 1d$	3.96	A_1, A_2, B_1	1	3140 $\overset{\circ}{\text{A}}$
$^1\Sigma^+ 1d$	4.62	A_1	1	2680 $\overset{\circ}{\text{A}}$
$^3\Sigma^+ 1s$	5.22	A_1	3	2380 $\overset{\circ}{\text{A}}$
$^1\Delta^+ 1s$	6.20	A_1, A_2, B_1	1	2000 $\overset{\circ}{\text{A}}$
$^1\Sigma^+ 1s$	6.86	A_1	1	1810 $\overset{\circ}{\text{A}}$

****Courtesy of W. H. Eberhardt, Georgia Institute of Technology.
 For explanation of symbols see H. Spomer and E. Teller, "Electronic Spectra
 of Polyatomic Molecules," Rev. Mod. Phys., 13:76, 1941.

maximum being either shifted towards the blue or suppressed as in the ozone case. Also, the intensity of absorption of bromine in carbon tetrachloride was found to be greater by a factor of 1.3 than that of gaseous bromine, while the contours and location of absorption are unchanged. It was concluded that since the 4150 \AA maximum was the more strongly affected of the two, a transition of the $^1\Pi - ^1\Sigma$ type is influenced to a greater extent than a $^3\Pi - ^1\Sigma$ transition. It is thought that the increased absorption coefficients are due to a combination of the Lorentz effect and an induced predissociation of the bromine singlet-singlet state by way of a triplet state. The Lorentz effect, which increases the absorption intensities of all transition types alike by a factor of 10%, is dependent upon the refractive index of the solvent.

The diffuseness of the visible spectrum of ozone gas would indicate that some type predissociation takes place, but as the absorption coefficients are increased in solution by a factor of five, the overall increase can not be attributed to this cause and the Lorentz effect alone. The singlet-singlet transition of bromine is an allowed transition while the singlet-triplet transition of ozone is forbidden. This fact would suggest that the singlet-triplet selection rule has been relaxed through the influence of the solvent molecules on ozone. As the transitions in the ultraviolet region are allowed, no great increase in absorption would be expected. This fact is substantiated experimentally in Figure 6 where it can be seen that in the lower wave length regions the absorption coefficients of ozone in carbon tetrachloride are comparable to those of the gas. Rough measurements performed by Eberhardt⁽²⁶⁾ in the 2500 \AA region show no great increase in absorption coefficients for ozone in

carbon tetrachloride.

In water the 5721 Å transition is influenced to a greater extent than the 6009 Å transition, while the two transitions are increased equally in carbon tetrachloride. It is thought that the geometrical properties of the excited state of ozone are such that a transition leading to the 5721 Å maximum is more probable than one leading to the 6009 Å maximum.

It might also be worth mentioning the smaller maxima occurring at 4839 Å, 5050 Å, and 5355 Å. In carbon tetrachloride solution these maxima seem to be affected to the same degree as those at 5721 Å and 6009 Å. This fact would indicate that the three lesser maxima can be attributed to the same type transitions. As the visible spectrum has been found to be temperature insensitive⁽²⁷⁾ it is difficult to attribute the maxima to transitions from excited vibrational states. Transitions from the ground vibrational state to various vibrational levels in the upper states would exhibit higher intensities at the lower wave lengths according to the Franck-Condon principle. It is interesting, however, that the energy difference between certain maxima is 2100 cm^{-1} , a fact which might suggest the nature of vibrational frequencies in the excited states. See Figure 8. As our measurements in water were not of sufficient accuracy to study the smaller maxima, it was impossible to determine which of these were suppressed in water solution.

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