

## The Absorption Spectrum of Ozone in the Visible I. Examination for Fine Structure. II. The Effect of Temperature

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and  $t_0 = T_0 - 273.16 = 20^\circ, 40^\circ, 60^\circ\text{C}$ , the results summarized in Table IX.

Additional data (for pure water) used in Eqs. (II-1) and (II-4) were

$$B(t) = 2.996 + 7.285 \times 10^{-3}(t - 25) - 1.790 \times 10^{-4}(t - 25)^2 + 6.13 \times 10^{-7}(t - 25)^2 \text{ kilobars},^{13}$$

and

$$\frac{1}{2.303} \frac{\partial \log v(0, 273.16 + t)}{\partial t} = \frac{2(t - 3.98)}{244,860 + 15,040(t - 3.98)^{0.62}} \frac{(0.62)(15,040)(t - 3.98)^{1.62}}{[244,860 + 15,040(t - 3.98)^{0.62}]^2}$$

obtained from Ipatov's<sup>16</sup> empirical equation for  $v$  by differentiation.

The average value of  $n$  is 7.146. In the present calculations this value has been rounded off to 7.15.

The entries in Tables IV, V, and VI therefore contain more significant figures than the test justifies. On the basis of the test, the errors associated with the use of the modified Tait equation are of the order of several percent. In

<sup>16</sup> I. V. Ipatov, J. Phys. Chem. (U.S.S.R.) 5, 1230 (1934).

particular, the results obtained for low pressures will disagree with known data by several percent.

### APPENDIX III

#### Symbols

$A[S]$  = parameter in modified ("adiabatic") Tait equation-of-state.

$B(t)$  = parameter in isothermal Tait equation-of-state.

$c$  = local velocity of sound.

$c_0$  = velocity of sound at zero pressure.

$c_p$  = specific heat at constant pressure.

$h$  = dissipated enthalpy increment:  $\int_{T_0}^T c_p(0, T') dT'$ .

$\Delta H$  = enthalpy increment:  $\Delta H = \omega + h$ .

$n$  = characteristic constant in Tait equation-of-state.

$p_0$  = initial pressure ahead of shock front,  $p_0 = 0$ , in these calculations.

$p$  = pressure behind shock front.

$S$  = entropy.

$s$  = sea water salinity.

$t$  = temperature in  $^\circ\text{C}$ .

$T$  = absolute temperature.

$u$  = particle velocity behind shock front.

$U$  = shock front propagation velocity.

$v_0$  = specific volume of medium ahead of shock front.

$v$  = specific volume of medium behind shock front.

$\bar{\beta}_0$  = mean compressibility at zero pressure over temperature range  $\Delta T$ .

$\rho$  = density.

$\sigma$  = Riemann function:  $\int_{p_0}^p \frac{v[p', S]}{c[p', S]} dp'$ .

$\omega$  = undissipated enthalpy increment:  $\int_{p_0}^p v[p', S] dp'$ .

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## The Absorption Spectrum of Ozone in the Visible

### I. Examination for Fine Structure. II. The Effect of Temperature

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(Received July 18, 1947)

The absorption spectrum of ozone in the visible spectral region has been investigated for fine structure and for changes in absorption with temperature. No fine structure was observed in spectrograms taken in the second order of a 21-ft. grating spectrograph. The absorption coefficients remained constant within experimental error in going from room to dry-ice temperature.

#### INTRODUCTION

THE effect of temperature on the absorption of ozone in the visible region of the spectrum has been the subject of considerable study, the results of which have been conflicting. In

1880 Chappuis<sup>1</sup> discovered the visible absorption bands of ozone and two years later published observations on the change in this absorption when the ozone was cooled from room temperature to  $-50^\circ\text{C}$  by rapid evaporation of methyl

\* Contribution No. 1140 from the Gates and Crellin Laboratories of Chemistry.

<sup>1</sup> J. Chappuis, Comptes Rendus 91, 985 (1880); *ibid.* 94, 858 (1882); Ann. de l'école normale sup. 11, 137 (1882).

chloride. He reported a marked increase in the intensity of absorption upon lowering the temperature. More recently, Lefebvre<sup>2</sup> photographed the visible spectrum of ozone at room and dry-ice temperatures, finding that the absorption did not change with temperature. Still later, E. Vassy<sup>3</sup> carried out investigations which confirmed Chappuis' qualitative results. Vassy also published values for the absorption coefficients of ozone in the visible at  $-40^{\circ}\text{C}$ ,  $-80^{\circ}\text{C}$ , and  $-100^{\circ}\text{C}$ .

It is important to know if there is an appreciable effect of temperature on the absorption of ozone, since this would influence photometric determinations of the amount of ozone in the atmosphere.<sup>4</sup> The results of such determinations are of considerable interest because of their meteorological significance.

The absorption of ozone in the visible has been studied under low dispersion by Wulf<sup>5</sup> and shown to consist of diffuse bands overlying a background of rather general continuous absorption. The two bands at approximately  $\lambda 5730$  and  $\lambda 6020$  are especially strong and broad. These bands fall in a region of the spectrum where glass optics may be used and where the intensity of solar radiation is high. In view of these facts the bands should be particularly adapted to a study of ozone in the atmosphere either by photographic or photoelectric methods, provided the intensity of their absorption is not too weak.

Cabannes and Dufay<sup>6</sup> have shown that the fractional absorption of atmospheric ozone in the orange-yellow bands is sufficiently high for photometric or bolometric measurements, and some use has been made of these bands in estimating the amount of ozone in the atmosphere.<sup>7,8</sup> However, the bands have not been used to their greatest advantage in the study of atmospheric ozone because the fractional absorption is small in comparison with that in the ultraviolet or infra-red bands, and also because

of the uncertainty as to whether there was a temperature effect.<sup>9</sup> Since modern photoelectric methods are quite capable of measuring with reasonable accuracy a small fractional absorption of the order of that caused by atmospheric ozone in the visible spectral region, it has seemed profitable to undertake a reinvestigation of the temperature effect in order to resolve the existing discrepancies.

The bands in the visible region of the ozone spectrum have always been described as being diffuse, but so far as we are aware they have not been investigated under more than moderate dispersion. If these bands should contain fine structure the absorption would undoubtedly show some dependence on pressure, thereby making it necessary to take this fact into account when using the bands for determinations of ozone. It has consequently seemed desirable to settle the question of fine structure definitely by obtaining spectrograms under high dispersion and resolution.

### I. Examination for Fine Structure

The possibility that fine structure is present in the broad bands at  $\lambda 5730$  and  $\lambda 6020$  was investigated by means of a 21-ft. grating spectrograph using a six-meter absorption cell containing 4 percent ozone by volume. The ozone was prepared and the concentration estimated in the manner described in Section II of this paper.

Spectrograms were taken in the second order with an average dispersion of about one angstrom per millimeter. The weak iron lines (third order)  $\lambda 3878.676$  and  $\lambda 3878.736$  near the strong line  $\lambda 3878.575$  were clearly resolved in the iron spectrum used as reference, but no structure was observed in the ozone bands.

An indication of the average spacing of lines which might be expected in an ozone band having structure may be obtained from observations in the infra-red. Average spacings of  $1\text{ cm}^{-1}$ <sup>10,11</sup> and  $5.7\text{ cm}^{-1}$ <sup>12</sup> have been reported in the infra-red bands. Even the former of these would correspond to a separation of about  $0.4\text{A}$  in the visible region and should certainly have been resolved under the conditions described above.

<sup>2</sup> L. Lefebvre, *Comptes Rendus* **200**, 653 (1935).

<sup>3</sup> E. Vassy, *Thesis de Doctorat, Serie A*, No. 1695, Paris (1937).

<sup>4</sup> For an excellent review on atmospheric ozone, methods of measurements, etc., see: F. W. P. Götz, *Ergeb. d. kosmischen Physik* **I**, 180 (1931); *ibid.* **III**, 253 (1938).

<sup>5</sup> O. R. Wulf, *Proc. Nat. Acad. Sci.* **16**, 507 (1930).

<sup>6</sup> J. Cabannes and J. Dufay, *J. de phys. et rad.* **7**, 257 (1926).

<sup>7</sup> F. E. Fowle, *Smith. Misc. Coll.* **81**, 1 (1929); *Trans. Am. Geophys. Union*, Part I, 164 (1935); J. Gauzit, *Thesis de Doctorat, Serie A*, No. 1569, Paris (1935).

<sup>8</sup> G. Dejaridin, A. Arnulf, and R. Falgon, *Comptes Rendus* **205**, 1086 (1937).

<sup>9</sup> See reference 4, **III**, 259.

<sup>10</sup> A. Adel, *Astrophys. J.* **94**, 451 (1941).

<sup>11</sup> S. L. Gerhard, *Phys. Rev.* **42**, 622 (1932).

<sup>12</sup> A. Adel and D. M. Dennison, *J. Chem. Phys.* **14**, 379 (1946).

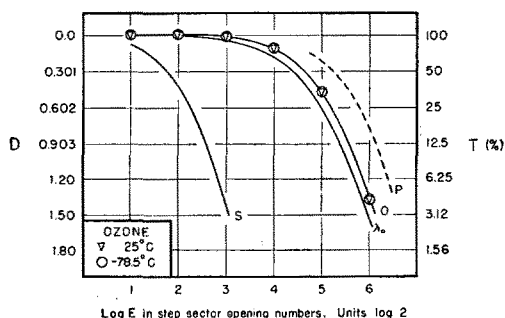


FIG. 1. Plot of density,  $D$ , against log "effective intermittent exposure,"  $\log E$ , for the  $\lambda 6020$  band. Curve S: cell containing oxygen;  $\lambda_0$ : intensity standard,  $\lambda 4300$ ; O: cell containing the ozone-oxygen mixture at two temperatures; P: predicted for the ozone-oxygen mixture at the low temperature by use of Vassy's absorption coefficients for  $-80^\circ\text{C}$ .

## II. The Effect of Temperature

The absorption was studied under low dispersion at room ( $25^\circ\text{C}$ ) and dry-ice ( $-78.5^\circ\text{C}$ ) temperatures in the region  $\lambda 3900$  to  $\lambda 6800$  by means of a Bausch and Lomb quartz spectrograph. A dispersion of about 57Å per mm was obtained in the region between  $\lambda 4500$  to  $\lambda 6050$  from which four bands were chosen for comparison of absorption at the two temperatures.

Ozone was prepared from tank oxygen by means of ice-water cooled, Siemens-type ozonizers. The rate of oxygen flow, as determined by a flow meter containing dibutyl phthalate, was 80 ml per minute. Traps containing dry-ice alcohol mixtures were provided before and after the ozonizers to dry the oxygen and to condense small amounts of oxides of nitrogen which might have been produced<sup>13</sup> in the ozonizers from traces of nitrogen in the tank oxygen. Oxides of nitrogen influence the decomposition of ozone and might contribute to the absorption in this region.<sup>14</sup> The entire apparatus was constructed from Pyrex glass, and all connections were made using ground-glass tapered joints partially lubricated with Apiezon M so as to minimize contact with ozone, although no reaction between the two was apparent.

The absorption cell, which consisted of a glass tube 3 meters in length and 1.5 centimeters in diameter with small diameter side-arm openings near each end, was filled by flowing the ozone-oxygen mixture through the tube. After about an hour, when a steady state was assumed to

have been achieved, the tube was sealed by closing stopcocks near the cell in the side arms, and a series of exposures was made on the enclosed ozone alternately at room and dry-ice temperature. Cooling the gas to dry-ice temperature was accomplished by surrounding the tube by a trough filled with carbon-dioxide snow. A period of a half-hour was found sufficient to allow the tube to come to thermal equilibrium with its surroundings. Estimations of the amount of ozone in the path using absorption coefficients of Colange<sup>15</sup> (in the manner to be outlined later in the discussion) gave approximately 6 percent ozone by volume. The maximum decomposition observed during any series of exposures amounted to about 2 percent of the total amount of ozone present initially, and usually no appreciable decomposition was observed during a period of about five hours.

A 500-watt tungsten projection lamp was used as source. The light emerging from the absorption cell was reflected to the slit of the spectrograph where it was interrupted by means of a rotating logarithmic-stepped sector which had six steps successively increasing in angular aperture by a factor of two. Uniform illumination of the slit was obtained by means of a cylindrical lens placed before the sector.

By shifting the position of the film in the plate holder it was possible to obtain as many as four spectrograms on a single film, thus affording a comparison of spectrograms developed simultaneously under identical conditions on the same emulsion. Each set of four spectrograms always included two spectrograms at one temperature and at least one at the other temperature. In some cases the fourth spectrogram was of the blank tube containing oxygen only.

Eastman type IV-F plates or process Panchromatic film were used to photograph the spectra. The mercury-arc spectrum was used as reference. Spectrograms of the ozone spectrum obtained in our investigations were similar in appearance to those published in Wulf's paper.<sup>5</sup>

Density measurements of plate blackening were made from microphotometer traces of the spectrograms, and the density data so obtained were treated as though they had been obtained by the use of a neutral step weakener in front of the spectrograph slit. The validity of this pro-

<sup>13</sup> See, for example, J. F. Schultz and O. R. Wulf, *J. Am. Chem. Soc.* **62**, 2980 (1940).

<sup>14</sup> E. J. Jones and O. R. Wulf, *J. Chem. Phys.* **5**, 873 (1937).

<sup>15</sup> G. Colange, *J. de phys. et rad.* **8**, 254 (1927).

cedure has been well discussed,<sup>16</sup> and it has been shown that residual errors caused by failure of the intermittent exposure to compensate for reciprocity law failure are of the order of accidental errors inherent in photographic photometry.<sup>17</sup>

A plot of density,  $D$ , against  $\log$  "effective intermittent exposure,"  $\log E$ , of the corresponding steps of the sector produces a curve similar to the well-known density-log energy curve. If conditions of development, exposure time, etc., are identical, curves obtained at different intensity levels are parallel—at least in the middle portions of the curves—and their displacement along the axis of  $\log$  "effective intermittent exposure," or opening number of the sector step to which  $\log E$  is proportional, is a measure of relative intensities.

To secure ideal conditions for photographic photometry, spectrograms of blank and filled absorption tubes at the two temperatures should be photographed simultaneously, side by side, on the same film. Since this was not practical a secondary reference of intensity was chosen which was always photographed simultaneously with the absorption regions, namely, the region  $\lambda 4300$  at which ozone absorption is negligible. The use of this reference permitted all spectrograms taken on one and the same film to be compared directly, since it eliminated possible errors caused by fluctuations of intensity of the source, or slight inequalities of exposure times.

The use of the  $\lambda 4300$  region as a reference is, of course, only strictly valid for exposures made on one and the same film, and consequently developed under identical conditions. However, development conditions were sufficiently well reproduced in our work so that the  $D-\log E$  curves from different films were essentially parallel, and since direct comparisons of the tube containing ozone at the two temperatures could always be made on one and the same film, we believe that serious errors could not have arisen.

The following method was used in comparing two spectrograms on the same film or on different films. The  $D-\log E$  plots for the two cases were superposed so that the curves for the  $\lambda 4300$  region coincided. The distance parallel to the  $\log E$  axis between two curves corresponding to any other spectral region of interest was taken

as proportional to the difference in absorption coefficients for the two cases, as represented by the equation:  $\Delta \log E = \log I_2 - \log I_1 = x \Delta \alpha$ . The units of  $\alpha$  are  $\text{cm}^{-1}$ , and  $x$  is the path length in cm of pure ozone at N.T.P. The amount of ozone in the path was determined from the transmission of the tube at room temperature by use of Colange's values for  $\alpha_{10}$  at  $20^\circ\text{C}$ . The average transmission of the ozone mixtures used in our experiments was about 0.14. When necessary, a correction for change of ozone concentration with time was made when comparing absorption at the two temperatures. In effect, the ozone concentration during a cold exposure was taken to be the mean of the concentrations during the exposures immediately preceding and following taken at the other temperature.

Figure 1 presents the average of the data for the band at  $\lambda 6020$ , and illustrates the method by which all data were treated.

Table I presents Colange's values for  $\alpha_{10}$  at  $20^\circ\text{C}$ , the change expected from calculations based on Vassy's data, and the results from three determinations for the change in absorption coefficients obtained in the present investigation in going to the lower temperature. It should be remarked that Vassy<sup>8</sup> employed Colange's values for  $\alpha_{10}$  at  $20^\circ\text{C}$  to obtain values for his absorption coefficient at dry-ice temperature, and that Colange<sup>15</sup> estimates his values of  $\alpha_{10}$  at  $20^\circ\text{C}$  to be good to 5 percent.

The small variations in absorption which we observe in going from room to dry-ice temperature are not systematic, and are well within the limits of probable errors inherent in photographic photometry. We believe that our experiments show definitely that the absorption of ozone in the visible region of the spectrum is not sensibly temperature dependent.

TABLE I. Changes in absorption coefficients for ozone\* in going from room to dry-ice temperature.

$\lambda$	Colange $\alpha(20^\circ\text{C})$	E. Vassy* $\Delta\alpha/\alpha \times 100$	Present work $\Delta\alpha/\alpha \times 100$			
			1	2	3	Average
6020A	0.050	+18.8	0.0	0.0	+1.0	+0.3
5730A	0.046	+20.7	0.0	-1.7	+1.4	-0.1
5317A	0.033	+14.6	-3.4	-6.0	0.0	-3.1
5053A	0.016	+ 7.5	—	-4.9	+4.1	-0.8

\* E. Vassy's data are presented in graphical form and the wave-lengths of the maxima do not agree with those found by other investigators or by us. The disagreement appears to be due to some error in the scale of wave-lengths used on his graph. From the trend of absorption with wave-length it is possible, however, to identify the bands; the values given in column three of Table I are calculated for regions which certainly correspond to the wave-lengths given here.

<sup>16</sup> R. A. Sawyer and H. B. Vincent, *J. Opt. Soc. Am.* **33**, 247 (1943).

<sup>17</sup> R. Breckpot, *Spectrochimica Acta* **1**, 137 (1939); J. H. Webb, *J. Opt. Soc. Am.* **23**, 157 (1933).

It is difficult to explain the previous conflicting results from experiments on cooling the ozone because of lack of sufficient detail about the manner in which the experiments were performed and the spectrograms evaluated. It is perhaps significant that in those cases<sup>1,3</sup> where an increase in absorption was reported after cooling, high concentrations of ozone were used in the absorption cell. Absorption coefficients published by A. Vassy<sup>18</sup> for the visible bands using a 50 percent ozone-oxygen mixture in the path are approximately 30 percent higher than those of Colange, who used 4 percent ozone by volume. Colange determined the concentration of ozone in his work by chemical analyses, while A. Vassy based her determinations of concentration on the absorption in the ultraviolet bands using absorption coefficients determined by Ny and Choong,<sup>19</sup> who employed concentrations of ozone varying from 2-6 percent by volume (chemical analyses).

It should be remarked that the concentration of ozone in the atmosphere is greatly below that used in the experiments described here. Consequently, if there is a temperature effect which

<sup>18</sup> A. Vassy, *Comptes Rendus* **204**, 1413 (1937); *ibid.* **206**, 1638 (1938).

<sup>19</sup> Ny-Tsi-Ze and Choong-Shin-Piaw, *Chinese J. Phys.* **1**, 38 (1933).

becomes apparent only at ozone concentrations considerably higher than we have employed in our work, then this effect would not render the visible bands unsuitable for determining atmospheric ozone.

### CONCLUSIONS

Although the reduction of intensity of solar radiation by the ozone of the atmosphere is small in the visible region of the spectrum, modern photoelectric methods are quite capable of measuring such weak absorption. Moreover, in view of the broad and continuous character of the absorption in the visible ozone bands, the relative simplicity of photometry in the visible region compared with other regions of the spectrum, and the absence of any uncertainty from effects of temperature or pressure on the bands, it seems likely that they will find further application in the measurement of atmospheric ozone.

### ACKNOWLEDGMENT

We wish to express great appreciation to Dr. Oliver R. Wulf of the U. S. Weather Bureau for bringing our attention to the investigations herein considered, and for his encouragement and very helpful discussions throughout the course of the work.

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## Ignition of Explosive Gas Mixtures by Electric Sparks. I. Minimum Ignition Energies and Quenching Distances of Mixtures of Methane, Oxygen, and Inert Gases\*

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(Received June 6, 1947)

An apparatus and experimental procedure is described for measuring capacitances and gap voltages of condensed electric spark circuits for sparks just powerful enough to ignite explosive gas mixtures. Mixtures of methane, oxygen, and inert gases are investigated. From the measured capacitances and gap voltages the minimum ignition energies are calculated. These energies are found to be independent of gap voltage. With increasing gap length they attain a minimum at critical distances which mark the farthest penetration of the flame-quenching effect of the electrode material. Above the quenching distances the energies remain constant over some range which is governed by mixture composition and pressure. Energies measured in this range may be regarded as absolute minimum energies, as defined in a subsequent paper. Data of such minimum energies and of quenching distances are presented for mixtures at room temperature and pressures ranging from 0.2 to 1 atmosphere.

**C**APACITANCES and gap voltages of condensed electric spark circuits have been measured for sparks just powerful enough to

ignite various explosive gas mixtures. From these data *minimum ignition energies* have been calculated. Data on the quenching of ignition

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