PHYSICAL REVIEW VOLUME 186, NUMBER 1 5 OCTOBER 1969

Absorption Cross Sections of O_2 and O_4 between 2000 and 2800 Å

Shardanand

Electromagnetic Technology Division, National Aeronautics and Space Administration,
Electronics Research Center, Cambridge, Massachusetts 02139

(Received 17 February 1969)

The total absorption of radiation in the 2000–2800 Å region has been measured for O_2. The absorption does not follow Beer's law. The linear increase in the measured effective absorption cross section with rise in gas pressure is ascribed to the absorption caused by O_4. With methods developed and presented recently by the writer, the absorption cross sections of O_2 and O_4 are derived from total absorption measurements.

I. INTRODUCTION

Solar radiation between 2000 and 2800 Å penetrates the upper atmosphere of the earth, and is absorbed below 80 km in the Herzberg[1] weak system of oxygen bands, $^3\Sigma_g^- \to {}^3\Sigma_u^+$, and in an associated continuum attributed to the dissociation $O_2(^3\Sigma_g^-) \to O(^3P) + O(^3P)$. This absorption in the continuum is the main source of oxygen atoms in our atmosphere and contributes to the formation of ozone.[2] Absorption of oxygen in this wavelength region has been studied by many investigators.[3-9] In particular, Ditchburn and Young[9] investigated in detail the absorption of oxygen experimentally and theoretically and determined the absorption cross sections in the continuum up to 2500 Å. They used a photographic technique in their investigation, observed the pressure dependence on the absorption cross section of O_2, and suggested that it might be caused by the absorption of O_4.

We have little knowledge of cross sections of gases in which the formation of double molecules (resulting either from molecular association by van der Waals forces or by pairs of molecules forming a collision complex) causes significant attenuation of radiation, and thus a departure from Beer's law. Consequently, it was decided to reinvestigate the cross sections of O_2 in the wavelength region from 2000 to 2800 Å with a more accurate photoelectric technique, and, in particular, to determine the role of complex oxygen molecules.

II. EXPERIMENTAL DETAILS

The attenuation measurement technique is shown schematically in Fig. 1. The equipment used in the measurement procedure included a 0.3-m McPherson vacuum-ultraviolet-scanning grating monochromator; a hydrogen-discharge light source; a stainless-steel high-pressure absorption cell sealed at both ends with lithium-fluoride windows; and a photomultiplier tube used as the detector. A magnesium-fluoride-coated plane grating ruled with 1200 lines/mm and blazed in the first order at approximately 1500 Å was used. In this monochromator, the collimation of incident radiation at the grating and focusing of dispersed radiation at the exit slit are accomplished by reflecting mirrors A and B, respectively. The slits of the monochromator were each 40 μ wide and the resulting resolution was about 2.5 Å.

The light source (McPherson model 630) was a hydrogen-discharge tube with a capillary sealed with a magnesium-fluoride window. The capillary and the anode were cooled by circulating water; the cathode was air cooled. The source was operated in an ac discharge mode. The hydrogen gas was used directly from the cylinder, and the flow of the gas was regulated by a needle valve. The hydrogen pressure in the capillary was approximately 1000 μ. Under these experimental conditions, a strong hydrogen continuum was produced.

Ditchburn and Young[9] employed long pathlengths (5, 10, and 30 m) and pressures ranging from 0.2 to 5 atm because of the expected small cross sections. They did not use higher pressures in order to avoid the formation of the complexes O_4, O_6, etc. In the present study, on the other hand,

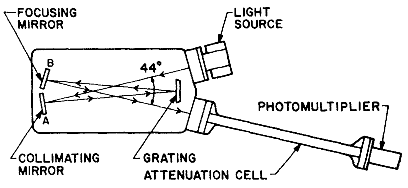

FIG. 1. Schematic diagram of the apparatus.

higher pressures favoring the formation of complexes, and consequently shorter pathlengths, were employed. Therefore, the absorption cell was made of stainless steel designed for use up to 100 atm. The pathlength in the cell (window-to-window) was 50 cm with a provision for extension to 100 cm. The cell was equipped with a pressure gauge (0–103-atm range), safety valve, inlet and outlet valves, and a port for connecting to the vacuum system. The cell was sealed at both ends with lithium-fluoride windows, $\frac{1}{2}$ in. thick and $1\frac{3}{4}$ in. in diam. The outer surface of the window facing the photomultiplier was coated with sodium salicylate. To measure the intensity, an EMI 9558Q photomultiplier with appropriate resistance loads was used. A voltage of 1000 V was applied to the dynodes of the photomultiplier from a regulated high-voltage supply (Fluke model 408B). The output of the tube was measured by a type 417 picoammeter (Keithley Instruments) and recorded by a Leeds and Northrup Speedomax W recorder.

III. PHOTOMETRIC STUDY

Laboratory grade 99.999% pure O_2, supplied by Liquid Carbonic Division of General Dynamics, was used directly from the tank. The gas was passed through multiple dry-ice cold traps before entering the cell. The spectrum was scanned at 20 Å/min and the chart speed was 1 in./min. A pathlength of 50 cm and gas pressures up to 24 atm were employed for the wavelength region from 2000 to 2350 Å, whereas, a pathlength of 100 cm and pressures up to 82 atm were used from 2100 to 2800 Å. It may be noted that the spectral region from 2100 to 2350 Å was investigated by using both pathlengths (see Table I).

First, the incident intensity $\Phi_0(\lambda)$ was measured; then the transmitted intensity $\Phi(\lambda)$ was recorded at various gas pressures. These intensity data were used to calculate the effective absorption cross section $\sigma_{\rm eff}(\lambda)$ defined by the expression

$$\sigma_{\rm eff}(\lambda) = (N_0 L)^{-1}(p_0/p)(T/T_0)\ln[\Phi_0(\lambda)/\Phi(\lambda)], \quad (1)$$

where N_0 is the Loschmidt number (2.687×10^{19} cm^{-3}), L is the pathlength (50 or 100 cm), p_0 and T_0 are standard pressure and temperature (273°K), and p is the pressure at $T = 298$°K. The cross sections thus obtained from Eq. (1) were found to increase linearly with increasing pressure of the gas and are plotted in Fig. 2 for some of the wavelenghs. Interpretation of this behavior is described in detail elsewhere.[10–12] Briefly, if one assumes that the increase of the absorption cross section is caused by the formation of O_4 molecules, then the present results may be interpreted as follows: Let $\sigma_1(\lambda)$ and $\sigma_2(\lambda)$ be the absorption cross sections of O_2 and O_4, respectively, and let K be the equilibrium constant which governs the formation of double molecules by the process

$$O_2 + O_2 \rightleftharpoons O_4 . \quad (2)$$

Then the behavior of $\sigma_{\rm eff}(\lambda)$, calculated from Eq. (1), may be represented by the expression[10]

$$\sigma_{\rm eff}(\lambda) = \sigma_1(\lambda) + K\sigma_2(\lambda)\, n , \quad (3)$$

where n is the number density of the gas. Equation (3) shows that the measured effective cross section increases linearly with n, which in turn is proportional to the pressure of the gas. It justifies the assumption that the interaction represented by the reaction (2) is the major contribution

TABLE I. Experimental determination of $\sigma_{\rm eff}(\lambda)$.

Wavelength (Å)	Pressure (10^6 dyn/cm^2)	Pathlength (cm)	Total gas column (10^{23} molecule/cm^2)	$\sigma_{\rm eff}(\lambda)$ (10^{-23} cm^2)
2350	13.79	50	1.47	4.3
	9.653	100	2.06	3.0
2300	19.306	50	2.06	7.4
	13.79	100	2.94	5.6
2250	17.927	50	1.91	8.8
	11.032	100	2.35	5.9
2200	11.032	50	1.18	7.6
	6.895	100	1.47	5.1
2100	9.653	50	1.03	7.9
	6.895	100	1.47	5.9

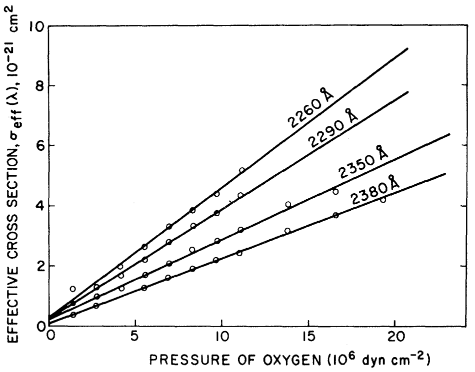

FIG. 2. Pressure dependence of the effective cross section of oxygen at selected wavelengths.

to the phenomenon observed; the higher-order interactions (O_6, O_8, $\cdots$) which will be proportional to the higher powers of pressure are insignificant.

We will now study the determination of $\sigma_1(\lambda)$ and $\sigma_2(\lambda)$. In Eq. (3), which represents a straight line, $\sigma_1(\lambda)$ is the value of $\sigma_{eff}(\lambda)$ at zero pressure, and $K\sigma_2(\lambda)$ is the slope. Therefore, $\sigma_1(\lambda)$ and $K\sigma_2(\lambda)$ can be determined by plotting the experimental values of $\sigma_{eff}(\lambda)$ against the gas pressure in the absorption cell. For this purpose, the values of $\sigma_{eff}(\lambda)$ were computed from Eq. (1) as a function of pressure. Over the spectral range covered by the measurements, $\sigma_{eff}(\lambda)$ was plotted to establish its linear dependence on pressure (see Fig. 2), and $\sigma_1(\lambda)$ was determined as shown in Fig. 3. For comparison, the values of $\sigma_1(\lambda)$ obtained by Ditchburn and Young[9] in the spectral range from 2000 to 2500 Å, using a photographic technique, are also shown in Fig. 3. It is seen that the values of $\sigma_1(\lambda)$ obtained here are higher. The discrepancy is probably caused by the differences in experimental technique. The absorption cross sections of O_2 reported here in the spectral range of the forbidden bands $^3\Sigma_g^- \rightarrow {}^3\Sigma_u^+$ (2500 to 2800 Å) have been measured for the first time. The values are probably too low at the maximum and too high at the minimum because of insufficient resolution of the monochromator. The experimental accuracy of the determination of $\sigma_1(\lambda)$, is estimated at ± 10% (3.8×10^{-25} cm^2 at 2500 Å), a quantity that is large compared with the Rayleigh scattering cross section (10^{-25} cm^2 at 2500 Å). Therefore, Rayleigh scattering may be neglected.

To calculate $\sigma_2(\lambda)$ from $K\sigma_2(\lambda)$, one must know the value of K. The equation of state[10] for a gaseous system in which reaction (2) is the only interaction between the molecules resulting in the formation of double molecules is

$$PV = NkT(1 - KN/V) , \quad (4)$$

where P, V, and T are, respectively, the pressure, volume, and temperature of the system; k is the Boltzmann constant; and N is the number of molecules in the system before the association begins. Comparison of Eq. (4) with the virial equation of state, namely,

$$PV = NkT(1 + BN/V + \cdots) ,$$

shows that the equilibrium constant K of reaction (2) is the second virial coefficient, if it is assumed that each pair interaction results in the temporary formation of O_4 molecules and higher-order interactions do not contribute to the present measurements. The value of K, calculated from the second virial coefficient for O_2,[13] is 2.48×10^{-23} cm^3/molecule at 300°K. It was used to calculate the values of $\sigma_2(\lambda)$ (as plotted in Fig. 4), from the slopes of the straight lines representing $\sigma_{eff}(\lambda)$ as a function of pressure. Also in Fig. 4 are plotted values of $\sigma_2(\lambda)$ derived by the writer from Ditchburn's published data.[9] In the spectral range from 2100 to 2500 Å, the two sets of values are in good agreement, but below 2100 Å, Ditchburn's data yield higher values. In the region from 2450 to 2800 Å, a series of diffuse bands, each consisting of three peaks, is shown. These bands were first reported by Finkelnburg and Steiner,[14] and their wavelengths, as indicated in Fig. 4 on the peaks of the bands, agree with present observations. Over the bands, pressure broadening may contribute to the apparent increase of cross sections with pressure. There is, therefore, some uncertainty regarding the accuracy of $\sigma_2(\lambda)$.

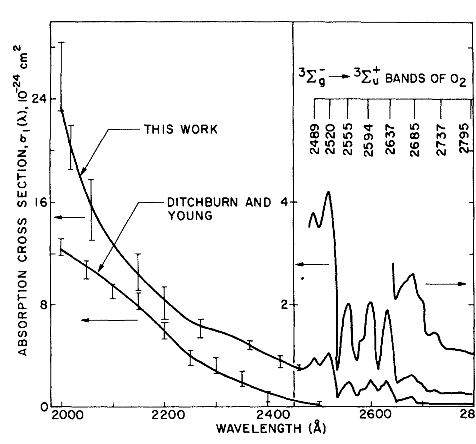

FIG. 3. Variation of the absorption cross section of O_2 with wavelength. Note the change of scale indicated by horizontal arrows.

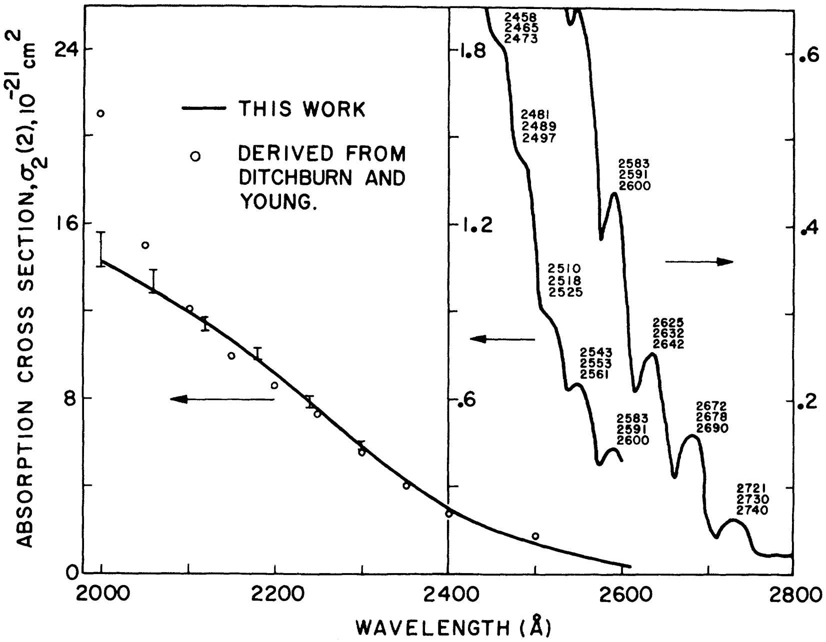

FIG. 4. Variation of the absorption cross section of O_4 with wavelength. Wavelengths shown on the peaks of the bands were first reported by Finkelnburg and Steiner (Ref. 14). Note the change of scale indicated by horizontal arrows.

IV. DISCUSSION

The quadratic dependence of the intensity of the bands between 2450 and 2800 Å on pressure and their diffuse nature suggests that they are due to loosely bound $(O_2)_2$ molecules.[4] There is also independent evidence[15–18] of the presence of O_4 in O_2 under various experimental conditions, namely, high pressure and/or low temperature. Further evidence of the existence of O_4 under the conditions of the present experiment is as follows: The absorption of incident radiation in the spectral region from 2100 to 2350 Å was measured as a function of pressure, with pathlengths of 50 and 100 cm. This particular spectral region was chosen because of the absence of absorption bands and associated complications of pressure broadening. The values of $\sigma_{\mathrm{eff}}(\lambda)$ obtained from these measurements are presented in Table I. As shown there, the values of total gas column at lower pressures and the longer pathlength are greater than those at higher pressures and the shorter pathlength. Nevertheless, the effective cross section is greater in the latter case. The presence of impurities cannot account for the observed pressure dependence, since its effect would be proportional to total gas column, resulting in an increase of $\sigma_1(\lambda)$. It might be argued, however, that O_2 is dissociated in the region of the continuum, leading to formation of ozone. In this manner, an appreciable quantity of ozone might accumulate in the pressure cell during an experiment lasting several hours, acting as an efficient absorber over the whole spectral range of the present study, with a broad maximum at 2550 Å. To establish the possible role of ozone, the following experiments were performed, using the pressure cell at an oxygen pressure of 20.5 atm. First, the absorption of incident radiation at 2550 Å was measured (since the dissociation limit of oxygen is at 2426.6 Å, no ozone can form at a longer wavelength). Then, after irradiation at 2000 Å for several hours, the absorption at 2550 Å was again measured. No change in absorption was observable between the two measurements at 2550 Å, which indicates that the ozone concentration was negligibly small. The conclusion – viz., that formation of O_4 molecules is the major factor for the observed pressure dependence of the absorption cross section – is therefore justified.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge with thanks the help of G. W. Grams in programming our calculations and of A. E. Barrington and J. A. Hull in preparing the manuscript. We also wish to thank Y. Tanaka for his critical reading of the manuscript and his comments. Thanks are also due to R. Ehrenbeck, M. Katzeff, and E. McCarthy for designing the high-pressure cell.

---

[1] G. Herzberg, Naturwissenschaften 20, 577 (1932).

[2] M. Nicolet and P. Mange, J. Geophys. Res. 59, 15 (1954).

[3] D. Chalonge and E. Vassy, Compt. Rend. Acad. Sci.

(Paris) 198, 1318 (1934).

[4] G. Herzberg, Can. J. Phys. 30, 185 (1952).

[5] H. P. Broida and A. G. Gaydon, Proc. Roy. Soc. (London) A222, 181 (1954).

[6] M. E. Pillow, Proc. Phys. Soc. (London) A66, 733, 1064 (1953).

[7] W. Heilpern, Helv. Phys. Acta. 14, 329 (1941).

[8] A. Vassy, Ann. Phys. (Paris) 11, 145 (1941).

[9] R. W. Ditchburn and P. A. Young, J. Atmospheric Terrest. Phys. 24, 127 (1962).

[10] Shardanand, Phys. Rev. 160, 67 (1967).

[11] Shardanand, J. Quant. Spectry. Radiative Transfer 8, 1373 (1968).

[12] Shardanand, NASA Report No. TN D-4225, 1967, (unpublished).

[13] A. S. Friedman, in American Institute of Physics Handbook, edited by Dwight E. Gray (McGraw-Hill Book Co., New York, 1963), 2nd ed.

[14] W. Finkelnburg and W. Steiner, Z. Physik 79, 69 (1932).

[15] G. N. Lewis, J. Am. Chem. Soc. 46, 2027 (1924).

[16] O. R. Wulf, Proc. Natl. Acad. Sci. U.S. 14, 609 (1928).

[17] W. Finkelnburg, Z. Physik 90, 1 (1934).

[18] V. I. Dianov-Klokov, Opt. i Spektroskopiya 16, 409 (1964); 17, 146 (1964); 20, 954 (1966); 21, 413 (1966) [English transls.: Opt. Spectry. (USSR) 16, 224 (1964); 17, 76 (1964); 20, 530 (1966); 21, 233 (1966)].

PHYSICAL REVIEW VOLUME 186, NUMBER 1 5 OCTOBER 1969

Measurement of the Hanle Effect for the OH Radical*

K. R. German† and R. N. Zare‡

Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colorado 80302

(Received 28 April 1969)

We have used the coincidence of the Zn I 3072.06 Å line with the $R_{12}(1)$ line of the (0, 0) band in the OH $A\,^2\Sigma^+ - X\,^2\Pi$ ultraviolet system to perform a measurement of the molecular Hanle effect on the $K' = 2$, $J' = \frac{3}{2}$ rotational level of the excited state. The OH was formed by the reaction $H + NO_2 \rightarrow OH + NO$, and the Hanle linewidth is extrapolated to zero pressure of H_2 and NO_2. The half-width is found to be 258 ±36 mG and the pressure broadening of the linewidth corresponds to 13 ±7 mG/mTorr of NO_2 pressure and 5.2 ±0.8 mG/mTorr of H_2 pressure. This linewidth gives a value of $g\tau = (2.20 \pm 0.27) \times 10^{-7}$ sec for this excited state of the OH molecule.

I. INTRODUCTION

The OH radical has long been a subject of intensive investigation because of its common occurrence in high-temperature sources such as flames, arcs, discharges, and even in our own sun.[1] Since the advent of microwave and ESR techniques the $X\,^2\Pi$ ground state of OH has been thoroughly studied,[2–8] yielding precise measurements of such quantities as its magnetic moment, Λ-type doubling and hyperfine splitting constants. No comparable measurements have been obtained for the first excited $A\,^2\Sigma^+$ state of OH,[9, 10] although recent observations of interstellar OH emission lines[11] have heightened interest in the detailed nature of the $A\,^2\Sigma^+$ state, which might explain the mechanism for population inversion found in the ground state.

Another related astrophysical application involving the $A\,^2\Sigma^+$ state of the OH molecule was pointed out by Crosley, Tango, and Zare[12] last year. The magnitude of the magnetic field associated with a comet is a matter of some controversy. It is believed that the cometary plasma interacts with the solar wind to form a shock front in which the interplanetary magnetic lines of forces are compressed and "frozen in." There is also speculation on the existence of an intrinsic cometary magnetic field. Crosley *et al.* propose that the cometary magnetic field can be measured through magnetic depolarization studies (Hanle effect)[13, 14] of molecular resonance fluorescence in comets. The half-width of the depolarization signal depends on the product $g\tau$, where g is the excited-state molecular g factor (analogous to the Landé g factor for atoms) and τ is the radiative lifetime. It was suggested that the OH $A\,^2\Sigma^+ - X\,^2\Pi_i$ ultraviolet-band system was particularly suitable for earth-based observation and might allow an upper limit of a few milligauss to be set.

Recently, Marshall, deZafra, and Metcalf[15, 16] have determined $g\tau$ for several different rota-