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ABSORPTION COEFFICIENTS OF O_4 AT OXYGEN WINDOWS

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SUMMARY

The attenuation coefficients of oxygen have been measured at O_2 windows. The attenuation does not follow Beer's law at four windows namely, 1215.7, 1187.1, 1157.0, and 1108.3 Å. The observed linear increase in attenuation coefficients with rise in gas pressure is ascribed to the formation of O_4 molecules. The absorption coefficients of O_4 are determined.

INTRODUCTION

Solar radiation penetrates down to the D layer through seven oxygen windows and plays an important role in the formation of the ionosphere. Therefore, great emphasis has been given by several investigators to the absorption coefficient of O_2 at these windows, specially at Lyman-α (1215.7 Å). The coefficients at O_2 windows were reported by Lee (ref. 1) and Watanabe (ref. 2). Preston (ref. 3) and Watanabe et al (ref. 4) reported a considerable pressure effect on the absorption coefficient at Lyman-α, using a photoelectric technique. Ditchburn et al (ref. 5) and Lee (ref. 1) observed no pressure effect by the method of photographic photometry. Recently Metzger and Cook (ref. 6) reinvestigated the absorption coefficient of molecular oxygen in the 1050- to 1800-Å region and reported the values at oxygen windows; they observed the slight pressure effect at Lyman-α. None of these investigators reported pressure dependence of the absorption coefficient at other oxygen windows and offered no satisfactory explanation of the pressure effect at Lyman-α. However, Preston (ref. 3) remarked that pressure broadening of molecular bands may account for this increase in the absorption coefficient with O_2 pressure.

It may be recalled that Ditchburn and Young (ref. 7) have observed the pressure dependence on the absorption coefficients of molecular oxygen between 2000 to 2500 Å and suggested that it might be because of O_4. The existence of O_4 (complex O_2 - O_2) has been established by the extensive work of Dianov - Klakov (refs. 8-11). In the present study, the absorption coefficients of O_2 have been reinvestigated at O2 windows and an explanation of the pressure dependence is advanced in terms of absorption caused by O_4. The absorption coefficients of O_4 are consequently determined experimentally.

RESULTS AND DISCUSSION

The attenuation measurement technique used in this experiment has been described elsewhere (ref. 12). Briefly, it consisted of a 2.2-meter normal-incidence vacuum ultraviolet monochromator equipped with a grating having 600 lines/mm and blazed in the first order at about 1500 Å. The light source was a conventional quartz capillary windowless hydrogen discharge. The intensity recording was accomplished with a sodium salicylate coated photomultiplier in conjunction with a micro-micro ammeter and a scanning recorder. The wave-length bandpass was 2 Å.

Assayed reagent-type oxygen gas supplied in 1-liter pyrex flasks was used. The vacuum system was equipped with appropriate multiple, dry-ice cold traps. The absorption cell was 10 cm long. First, the incident intensity $\Phi_o(\lambda)$ was measured and then the transmitted intensity $\Phi(\lambda)$ was recorded as a function of gas pressure in the cell. These intensity data were then utilized to calculate the effective attenuation cross section $\Phi_{eff}(\lambda)$ cm^2 defined by the expression:

$$\sigma_{eff}(\lambda) = \frac{1}{nL} \ln \frac{\Phi_o(\lambda)}{\Phi(\lambda)} = \alpha_{eff}(\lambda)/n_o \qquad (1)$$

where n is the number of absorbers/cm^3, L is the pathlength in cm, and n_o is the Loschmidt number. The attenuation coefficient $\alpha_{eff}(\lambda)$ is expressed in cm^{-1}. The coefficients thus calculated were found to increase linearly with increasing pressure of the gas at four oxygen windows, namely, 1215.7, 1187.1, 1157.0, and 1108.3 Å, and are shown in Figure 1. No pressure dependence was observed at the remaining three windows, namely, 1166.8, 1142.8, and 1126.9 Å, for pressures up to 400 mm Hg. In this pressure range, Beer's Law was obeyed within an experimental error of 10 percent. The pressure dependence of the absorption coefficient can be explained as being caused by the absorption of radiation by O_4 molecules, as follows:

On the assumption that the attenuation of radiation caused by scattering by O_2 and O_4 is negligible as compared with absorption, the pressure dependence of the attenuation coefficient $\alpha_{eff}(\lambda)$, calculated from Eq. (1), may be represented by a linear expression (ref. 12) of the form:

$$\alpha_{eff}(\lambda) = \alpha_1(\lambda) + K\alpha_2(\lambda)\, n \qquad (2)$$

where $\alpha_1(\lambda)$ and $\alpha_2(\lambda)$ are the absorption coefficients of O_2 and O_4, respectively, and K is the equilibrium constant which governs the formation of double molecules by the process:

$$O_2 + O_2 \rightleftharpoons O_4 \quad . \qquad (3)$$

It is clear from expression (2) that the absorption coefficient of O_2 is the value of $\alpha_{eff}(\lambda)$ reduced to zero pressure. Therefore, the absorption

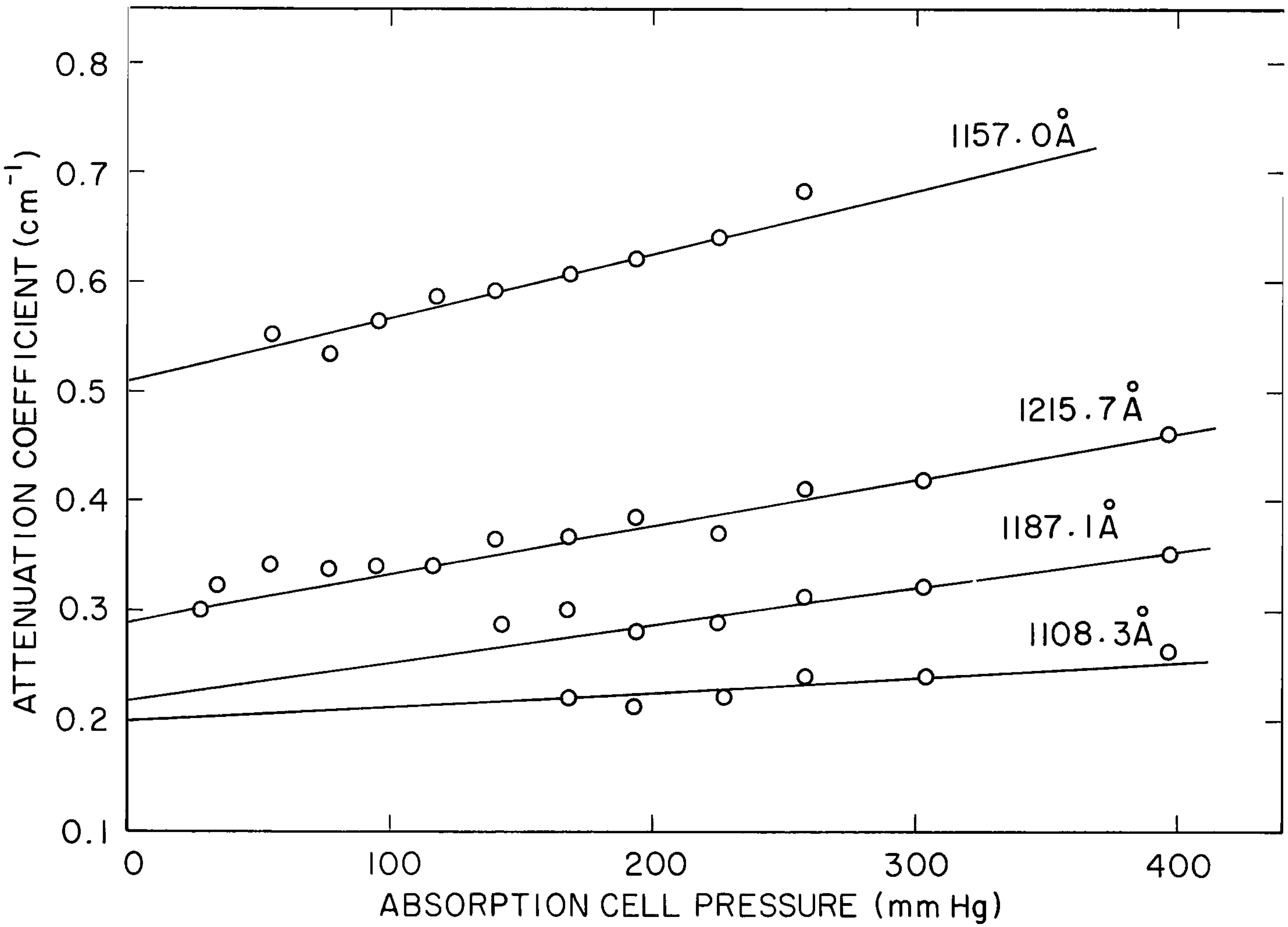

Figure 1. Pressure dependence of the absorption coefficient of O_2 at 1215.7, 1187.1, 1157.0, and 1108.3 Å

coefficients of O_2 at 1215.7, 1187.1, 1157.0, and 1108.3 Å were derived from Figure 1, corresponding to zero pressure. At 1166.8, 1142.8, and 1126.9 Å they were obtained directly from Eq. (1) and are given in Table I. For comparison, the values obtained by other investigators are also listed in the same table. Values of the coefficients at 1166.8 and 1142.8 Å are very high because of the poor resolution employed.

The slope of the straight line (Eq. (2)) is a measure of $K\sigma_2(\lambda)$. To calculate $\sigma_2(\lambda)$ from $K\sigma_2(\lambda)$, one must know the value of K. The equation of state for a gaseous system in which relation (3) represents the only interaction between the molecules is (ref. 12):

$$PV = NkT(1 + K\frac{N}{V}) \qquad (4)$$

where P, V, and T are 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,

$$PV = NkT(1 + B\frac{N}{V} + ----) \qquad (5)$$

shows that the equilibrium constant K of reaction (3) is the second virial coefficient if it is assumed that each pair interaction results in the temporary formation of O_4 molecules. The value -6.05×10^{-4}RT atm^{-1} at 300°K of the second virial coefficient has been reported by Hilsenrath et al (ref. 13). Therefore, the value of the equilibrium constant K at 300°K is 6.05×10^{-4} atm^{-1} or 2.49×10^{-23} cm^3/molecule, which has been utilized to calculate the absorption coefficients of O_4 at 1215.7, 1187.1, 1157.0, and 1108.3 Å from the respective slopes. At the other three windows, namely, 1166.8, 1142.8, and 1126.9 Å, where the pressure effect was not observed, only the upper limits could be determined; the results are presented in Table I. Because of the complex nature of the O_2 absorption in the region 1350 to 1050 Å, it is difficult to estimate how much pressure broadening of molecular bands may contribute to the change in absorption coefficient with pressure. Consequently, the values of the absorption coefficient of O_4 given in the last column of Table I might be higher than the true values.

As to the nature of the O_4 molecules, they are probably held together by van der Waals' forces, or exist as a collision complex. Whether they are singly or simultaneously responsible for the observed departure from Beer's Law needs further investigation.

TABLE I

ABSORPTION COEFFICIENTS OF O_2 AND O_4
AT OXYGEN WINDOWS

Wavelength	Absorption Coefficients				
	O_2				O_4
	This Work	Metzner & Cook	Watanabe	Lee	This Work
Å	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
1215.7	0.29 P	0.28	0.27	0.23	517.4
1187.1	0.22 P	0.20	0.18	0.35	418.1
1166.8	0.35	0.29	0.27	0.28	$<$106
1157.0	0.51 P	0.44	0.51		708.7
1142.8	0.43	0.31	0.26		$<$131
1126.9	0.62	0.62	0.53		$<$188
1108.3	0.20 P	0.20	0.11	0.44	168.5

P - Pressure-Dependent

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