ABSORPTION COEFFICIENTS OF O_2

IN THE VACUUM ULTRAVIOLET

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Prepared

for

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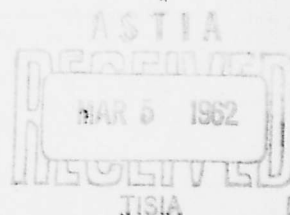Honolulu 14, Hawaii

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ABSTRACT

With a resolution of 0.2 A the absorption coefficients of O_2 were obtained for about 600 wavelengths in the region 840-1100 A and also at 584.3 A. The present method resolved band structures which were not detected by previous photoelectric measurements and at many wavelengths where comparison could be made the absorption coefficients agreed closely with the earlier data. Also with this improved resolution a pressure effect was observed for the pre-ionized H, H', M and M' bands.

Continua due to photodissociation and photoionization were observed in the absorption spectrum. Vibrational levels of the ion were inferred from the absorption spectrum.

Several absorption bands seem to form a limit at 1026.5 A, the position of the ionization potential obtained by a photoionization method. The extension to the shorter wavelength proved difficult; nevertheless, a Rydberg series $\nu_n = 97,418 - R/(n + 0.57)^2$ is tentatively suggested on the basis of several bands.

I. INTRODUCTION

A. General

The absorption bands of O_2 in the spectral region 600-1100 A were first studied by Hopfield.[1] Later several investigators[2,3] using higher dispersion have identified many prominent absorption bands as members of Rydberg series converging to the electronically excited states of O_2^+, but have failed to identify a Rydberg series converging to the ground state of the ion.

Although several investigators[4-7] have determined the absorption coefficients (k-values) of O_2 in the region 850-1100 A by means of photographic cr photoelectric photometry, there appear to be large discrepancies in published results. Quantitative k-values for this region are particularly important to establish the magnitude and range of continua due to photoionization and photodissociation, to obtain oscillator strengths, and to the theory on the formation of the atmospheric E layer.

The present study is an extension of our work[7,8] on O_2 using photoelectric photometry with an improved resolution of 0.2 A. The previous study[7] reported k-values obtained with 1 A resolution for 200 wavelengths, which were not uniformly quantitative due to lack of resolution. In the present study we have attempted to obtain quantitative k-values for many wavelengths and to identify a Rydberg series leading to the ground state of the ion.

B. **Definitions**

The absorption coefficient k in cm^{-1} is defined by the equation

$$I = I_0 \exp(-kx) \qquad (1)$$

where I_0 and I are the incident and transmitted light intensities and x in cm is the layer thickness of the absorbing gas reduced to NTP. When an absorption chamber of length L in cm contains gas at a pressure p in mm Hg and temperature T in °K, the layer thickness can be computed from

$$x = L. \frac{P \cdot 273}{760 \cdot T} \qquad (2)$$

The absorption cross section in cm^2 is defined by

$$\sigma = k/n_0 \qquad (3)$$

where n_0 equals 2.69×10^{19} particles per cm^3.

II. EXPERIMENTAL

A. Monochromator

A McPherson Precision Instruments Model 220, one-meter, normal incidence, vacuum monochromator was used in the present study. A 1200 lines per mm platinized grating[9] gave usable H_2 spectrum down to 840 A and also the He line at 584 A. Slit widths of 20 microns gave a band width of 0.17 A. The slit assemblies were mounted so that the gas flowed entirely through the slits.

B. Light Source

The light source was a windowless hydrogen discharge tube with a platinized quartz capillary using commercial tank H_2 and is similar to the source described by Johnson, et al.[10] A needle valve was used to control the H_2 flow rate, and the lamp was operated at 0.4 amp with 650 volts dc across the discharge tube. The light source was operated with He under similar conditions. Wavelengths of the H_2 emission spectrum were calibrated from photographic plates obtained by Dr. P. G. Wilkinson with a 7-meter spectrograph.

C. Absorption Cells

The windowless absorption cell was a cylindrical brass tube attached to the exit slit arm with an o-ring seal. The photoelectric detector was mounted behind the cell with an o-ring seal. Cell lengths used were 24.5 ± 0.05, 14.0 ± 0.05, and 3.57 ± 0.05 cm. An absorption cell, 10.5 ± 0.05 cm long, with LiF windows was used to obtain k-values needed in the

pressure calibration.

D. Detector

An EMI model 9514B photomultiplier mounted behind a sodium salicylate coated vacuum sealed glass window was used as the photoelectric detector. Voltages ranging from 800 to 1060 volts dc were applied across the detector with an Atomic model 312 power supply. The photomultiplier output current was measured by a RCA WV-84A microammeter and recorded on a Speedomax recorder.

E. Gas-Handling System and Gas Samples

The gas-handling system was provided with a Philips ionization gauge, silicone oil and mercury manometers, McLeod gauge, and a Consolidated Electrodynamics micromanometer model 23-105.

The gases O_2 and CO_2 used were obtained from Linde Gas Company and Matheson Company, respectively. Assayed reagent grade of O_2 was obtained in one liter pyrex flasks and compressed bone-dry grade CO_2 (99.8% minimum purity) was obtained in a metal cylinder.

F. Pressure Calibration

In a flow type absorption cell there may be a significant pressure differential so that pressure gauges are likely to give incorrect pressures. In order to obtain reliable pressure data, a technique similar to that of Watanabe and Marmo[7] was used. A Consolidated micromanometer and an oil manometer (depending on pressure range) were used as indicators, and the actual pressure in the cell was obtained by their absorption method.

The pressure in the flow cell was determined as follows: Using a cell with LiF windows, the k-values of O_2 at 1435.3 A and CO_2 at 1121.3 A were carefully measured and were found to be 394 cm^{-1} and 4640 cm^{-1}, respectively, with errors less than 5 percent. Then using a flow type cell, I_o and I at 1435.3 A were taken for O_2 flowing uniformly through the cell, and simultaneously, the micromanometer or oil manometer reading was recorded. The pressure was computed and related to the manometer reading. This was repeated for many pressures. Similar measurements were carried out with CO_2 at 1121.3 A. Since its k-value is about 12 times higher than that of O_2 at 1435.3 A, CO_2 was useful for low pressures.

The actual pressure in the cell as related to the manometer reading was obtained for about 150 points between 0.005 and 1.40 mm Hg.

G. Procedure

The light source and electronic equipment were warmed up for about an hour before measurements were taken. In order to minimize the error due to gradual changes in the light intensity, the spectral region between 850-1100 A was examined in 50 A intervals. The procedure used is as follows: (1) A suitable voltage for the detector was selected and a I_o trace was taken with a scanning speed of 2.5 A per min. (2) O_2 was flowed through the absorption cell and I was recorded with the manometer readings taken at about 2 A intervals. (3) The procedure was repeated with different pressures.

For the five 50 A intervals starting at about 850, 900, 950, 1000, and 1050 A the pressures ranged from 0.032-0.21,

0.020-0.33, 0.030-0.78, 0.055-1.00 and 0.140-1.10 mm Hg, respectively.

For all gas pressures used the monochromator chamber pressure was less than 10^{-4} mm Hg; thus by keeping a low chamber pressure, it was possible to keep the spectral intensity of the source constant to within 5 percent. Also this kept the layer thickness of the absorbing gas confined to the cell.

The recorder trace of I and I_0 showed the relative intensity for each wavelength since the detector used had a linear response. However, superimposed on the spectrum is the scattered light intensity which must be subtracted to give the corrected I or I_0. The scattered light correction was obtained by having a sufficient pressure of O_2 to cause total absorption for a wavelength with high k-value and recording the amount of scattered light transmitted.

The wavelength, temperature, corrected I and I_0, pressure, and cell length provided the data for equations (1) and (2). An IBM 650 computer was then used to calculate the k-values.

H. Sources of Error

The largest systematic error, about 10 percent, was due to uncertainties in the pressure measurements. The error due to fluctuation in the light source was estimated to be less than 5 percent. Therefore, errors of individual k-value may be as high as 15 percent.

III. RESULTS AND DISCUSSIONS

A. Absorption Coefficients of O_2 in the Region 840-1100 A

The absorption curves shown in Figs. 1 and 2 were obtained
by drawing a curve through about 600 points, each representing
a mean of several k-values which are tabulated in the Appendix.
The dashed portion in Fig. 2 represents the results from a
previous study.[8] The Rydberg bands (H,H',M,M' and I,I')[2,3]
and a suggested Rydberg series converging to the first ioniza-
tion potential (IP) are shown in Figs. 1 and 2, respectively.
The curves are consistent with published photographs[2,3] and
on the whole the k-values are in agreement with those obtained
by Lee[6] and Watanabe and Marmo.[7]

At the peak of the M and M' Rydberg bands an appreciable
pressure effect was observed. The k-values increased by 2
to 4 times with pressure changes of 0.33 to 0.02 and 0.78 to
0.03 mm Hg for the regions 900 to 950 and 950 to 1000 A,
respectively. The H and H' bands exhibited a smaller depend-
ency pressure. A previous study[7] found these bands to be
strongly pre-ionized and suggested that the pressure effect
may not be due entirely to the limited resolution of 1 A.
Since the effect is still large with 0.2 A resolution we
conclude that the pre-ionized bands are pressure dependent.
For the intense bands between 930 and 985 A the tabulated
k-value was a mean of several pressures between 0.02 and 0.08
mm Hg, and this mean was within 20 percent of the highest
k-value. For other wavelengths between 840 and 1000 A the
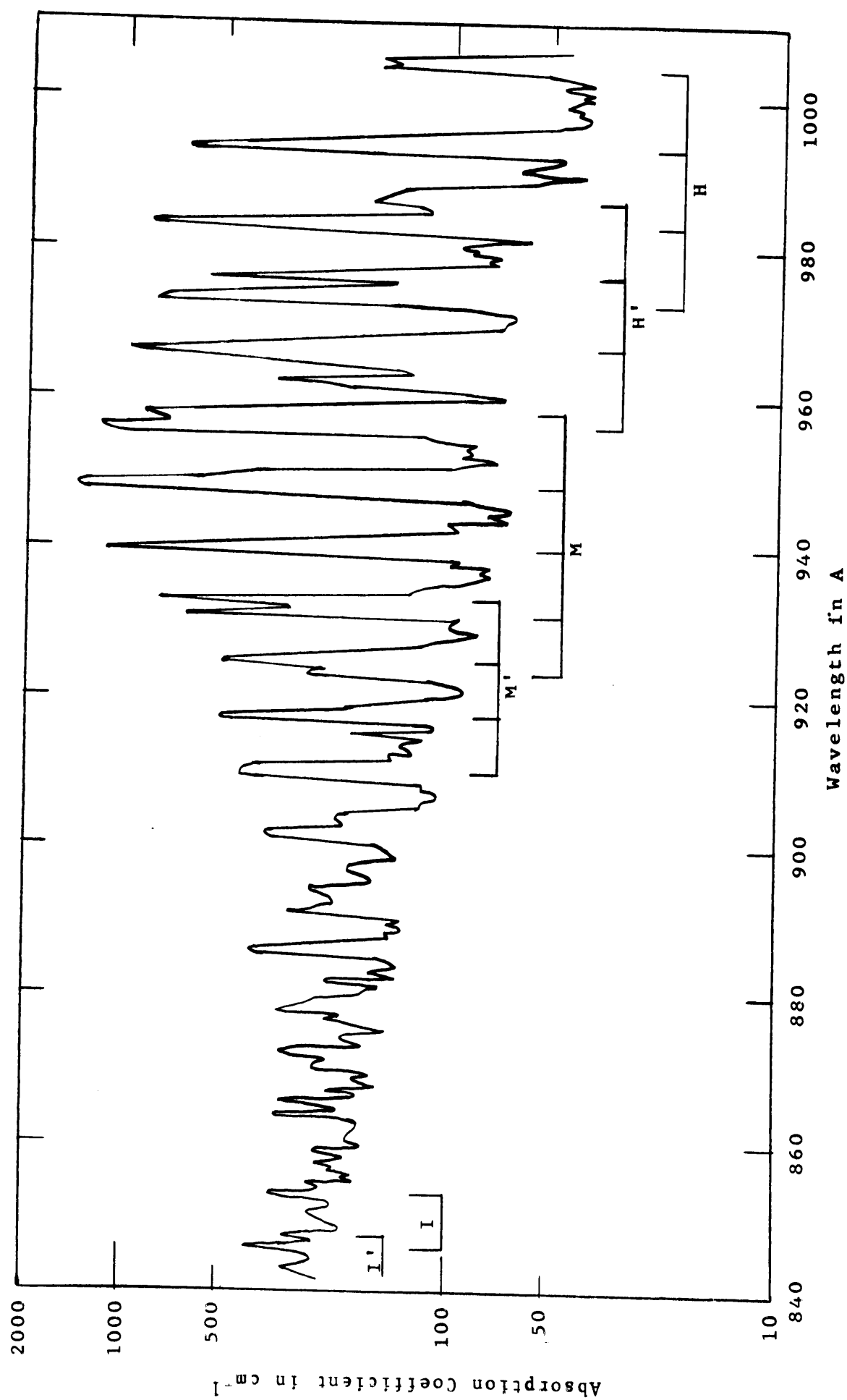
Fig. 1. Absorption coefficient curve of O_2 in the region 840-1010 A.
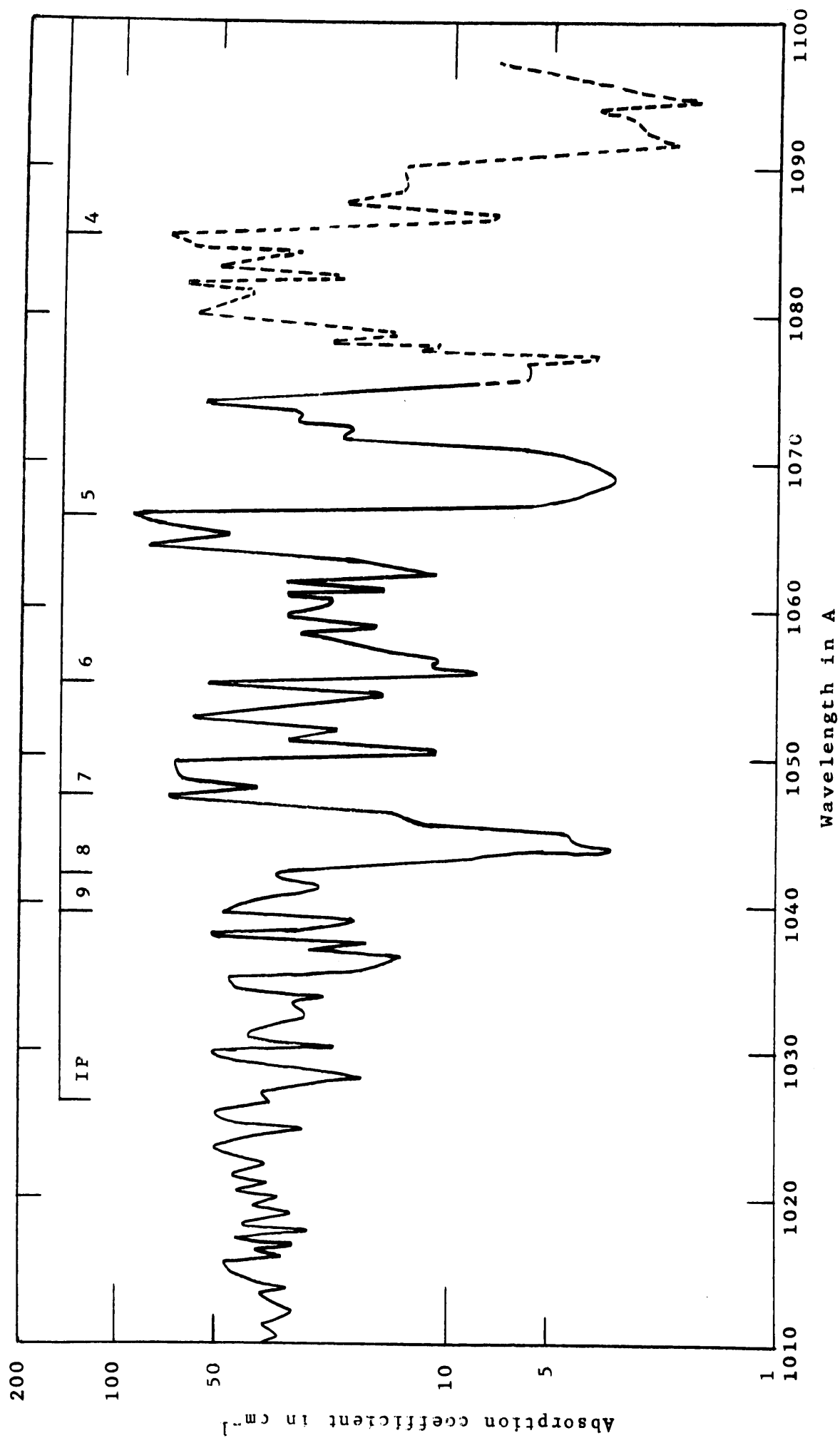
Fig. 2. Absorption coefficient curve of O_2 in the region 1010-1100 A.

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k-values were averages of the data taken with all pressures. The results are in good agreement with the values of Lee[6] but he reported no pressure effect at all for these bands.

In the region 1000-1100 A a pressure effect was observed for many wavelengths. For this region, when pressures greater than 0.1 mm Hg were used, the k-values were constant within the experimental limits, but with the lowest pressure used the k-values were as high as 3 times the constant value. Lee[6] observed no pressure effect while Watanabe and Marmo[7] reported a pressure effect. Since there are bands which are sharp and complex in this region, the discrepancy could be due to lack of resolution or the accuracy of the ratio of I_0/I for low pressures. The tabulated k-values are means of data taken with 4 different pressures greater than 0.1 mm Hg.

In the region 1030-1100 A where Rydberg series converging to the first ionizational potential are expected, the absorption spectrum is extremely complex. Several investigators[2,11] have attempted to identify a series and Tanaka[11] has classified several groups of bands, most of them shading toward the shorter wavelengths and some appearing diffuse. Using the ionization potential obtained by a photoionization technique, 12.08 ev, which corresponds to 1026.5 A,[7] several bands fit the Rydberg equation

$$\mathcal{V}_n = 97,418 - R/(n + 0.57)^2 \qquad n = 3 \text{ to } 9 \qquad (4)$$

This is a suggested Rydberg series since it is based on seven bands and the higher members were difficult to identify. A reliable series may be obtained with higher resolution and a continuous background source.

In this region there appears to be a weak dissociation continuum which was suggested by Price and Collins[2] to begin at about 1105 A. In Fig. 2 there are three minima at about 1095, 1069, and 1044 A. The k-value rises from 1095 to 1069 A and remains constant to 1044 A. This result agrees with Lee[6] who ascribed the continuum to the dissociation reaction

$$O_2 + h\nu \longrightarrow O(^1D) + O(^1S). \qquad (5)$$
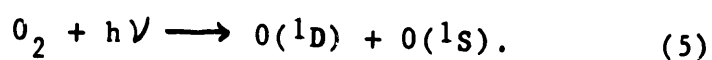
In the region 840-1030 A there appears to be a ionization continuum beginning near 1030 A with a minimum k-value of 18 cm^{-1}. The minimum k-value, which was independent of pressure, increases more or less progressively to 210 cm^{-1} at 850 A. Watanabe and Marmo[7] observed a similar continuum but Lee[6] obtained a continuum beginning near 1035 A with k-value of about 10 cm^{-1} and increasing gradually to 110 cm^{-1} at 920 A and then decreasing smoothly to 81 cm^{-1} at 850 A. Also a weak dissociation continuum is probably present since the photoionization yield averaged 85 percent for this region.[7] The stepwise rise in the continuum at 1026.5, 1007, 988, and 969 A, which correspond roughly to the expected intervals of the levels v = 0, 1, 2, 3 of the $X^2\Pi$ state, confirms the work of Watanabe and Marmo.[7] In the longer wavelength region the bands at about 1060, 1080, and 1102 are probably Rydberg bands leading to the vibrationally excited states of the ion at 1007, 988, and 969 A, respectively.

B. Absorption Coefficient of O_2 at 584.3 A (He I)

The mean k-value for O_2 at 584.3 A was 560 cm^{-1} and was independent of the pressure used (0.050 to 0.35 mm Hg). This is within 10 percent of all the published values except one.[4-6,12,13]

APPENDIX

Table I

Absorption Coefficients of O_2 in the Spectral Region 840-1075A

λ = wavelength in A

k = absorption coefficient in cm^{-1}

λ	k	λ	k	λ	k
841.9	240	858.1	210	873.6	180
43.6	310	58.5	250	73.8	200
44.6	250	59.5	180	74.3	210
45.3	260	59.8	180	75.1	150
46.1	410	60.3	200	75.8	170
47.1	250	62.1	190	76.2	200
47.4	310	62.6	180	76.7	230
48.0	210	63.4	200	77.4	210
49.1	210	63.7	330	77.8	320
49.7	230	64.3	210	78.7	280
50.2	250	64.7	240	79.0	260
50.6	260	65.1	320	79.5	220
51.0	240	65.6	210	80.1	180
51.5	220	66.0	190	80.6	170
52.2	230	66.2	190	81.0	160
52.8	320	66.9	230	81.7	230
53.2	340	67.4	160	82.1	140
53.5	270	67.9	170	82.5	170
54.1	240	68.5	190	83.3	150
54.5	260	69.0	170	83.5	140
54.9	190	69.5	200	84.1	150
55.3	200	69.9	240	84.5	160
55.7	190	70.3	250	85.0	230
56.1	220	71.4	230	85.2	350
56.4	220	71.7	270	85.8	400
57.0	240	72.1	320	86.5	260
57.9	200	72.9	190	87.2	180

λ	k	λ	k	λ	k
887.7	150	907.4	110	923.5	240
88.1	150	07.7	120	24.0	360
88.3	140	08.1	120	24.3	400
89.0	140	08.6	170	24.7	490
89.6	150	09.6	430	25.1	400
89.8	140	10.4	410	25.5	300
90.3	180	10.6	390	26.0	210
91.2	240	11.2	200	26.8	120
91.5	300	11.5	150	27.3	110
91.8	250	11.8	150	27.8	98
92.4	220	12.2	130	28.1	82
93.4	230	13.5	140	28.8	100
94.6	260	14.2	120	29.6	100
94.8	220	14.8	200	30.0	94
95.5	170	15.6	110	30.2	210
96.2	190	16.0	110	30.7	640
96.5	200	16.3	150	31.0	390
97.1	190	17.0	500	31.4	310
97.9	180	17.2	490	31.7	330
98.2	140	17.8	420	32.1	370
98.6	150	18.7	200	32.5	780
99.6	160	19.0	160	33.3	210
900.2	210	19.2	130	33.8	150
00.7	350	19.5	110	34.5	120
01.3	360	20.0	100	34.9	110
01.7	310	20.2	92	35.6	86
02.3	230	20.4	90	35.8	81
02.8	210	21.2	93	36.1	77
03.7	220	21.4	100	36.4	80
04.1	210	21.6	110	36.9	77
04.6	170	22.2	150	37.1	98
05.5	120	22.5	170	37.6	96
05.8	120	22.8	240	37.8	100
06.7	110	23.2	270	38.1	130

λ	k	λ	k	λ	k
938.8	850	956.7	750	974.1	210
39.3	1150	56.9	870	74.5	150
40.3	460	57.3	690	74.8	190
41.1	220	57.8	340	75.1	440
41.6	120	58.4	230	75.5	560
42.2	95	58.8	120	75.9	420
43.3	100	59.4	73	76.2	340
43.5	100	59.7	70	76.7	160
43.8	67	60.0	74	77.3	85
44.1	75	60.7	160	77.7	74
44.5	72	61.7	230	77.9	78
44.8	65	62.0	350	78.5	73
45.2	79	62.3	270	79.2	87
46.0	88	62.8	130	79.5	86
46.7	180	63.1	130	79.8	95
47.4	940	63.6	230	80.1	85
47.8	1400	64.1	260	80.5	58
48.1	1400	64.8	460	81.3	66
48.4	600	65.4	820	81.7	100
48.7	430	65.6	880	82.1	160
49.1	340	66.0	970	82.6	760
49.7	140	67.3	280	83.3	850
50.9	93	67.6	200	83.8	390
51.3	81	67.9	120	84.6	120
51.6	73	68.3	94	85.2	120
51.9	92	69.2	71	85.8	180
52.3	87	69.9	69	86.1	170
52.6	88	70.2	68	86.6	160
52.8	89	70.4	65	86.9	150
53.6	85	71.0	68	87.5	110
54.8	120	71.4	88	88.0	80
55.6	960	72.0	180	88.5	60
55.9	1200	72.5	820	89.3	53
56.5	740	73.4	770	89.6	40

λ	k	λ	k	λ	k
990.1	63	1005.0	83	1018.8	29
90.6	60	05.5	76	19.4	38
91.2	53	05.8	57	20.4	32
91.7	47	06.2	44	20.8	43
92.0	55	06.4	43	21.1	35
92.9	450	06.8	37	21.6	44
93.3	660	07.3	40	21.9	41
93.5	560	07.6	44	22.4	35
94.2	360	07.9	49	23.4	50
94.4	220	08.3	48	23.8	46
94.8	130	08.8	43	24.3	38
95.2	78	09.1	38	24.6	27
95.7	50	09.4	41	25.3	48
96.1	47	10.0	36	25.7	50
96.5	41	10.5	32	26.6	34
97.2	39	11.4	35	27.1	35
97.6	39	11.6	32	27.8	29
98.0	42	12.3	29	28.2	18
98.4	42	12.5	31	28.8	25
98.8	46	13.0	34	29.3	51
99.3	44	13.5	36	30.2	22
99.7	38	13.9	30	30.8	39
1000.0	40	14.2	37	31.0	40
00.7	38	14.5	42	31.3	39
00.9	41	15.4	46	31.9	32
01.5	47	15.8	47	32.3	27
01.9	38	16.0	32	33.1	29
02.4	41	16.4	37	33.6	24
02.6	55	16.9	29	34.3	43
03.2	120	17.2	43	34.9	45
04.0	170	17.8	26	35.5	18
04.3	150	18.3	41	36.5	14
04.6	170	18.6	34	36.9	26

λ	k	λ	k	λ	k
1037.2	18	1049.5	67	1062.0	16
38.0	51	50.1	11	62.6	11
38.2	29	50.6	15	63.4	20
38.8	19	51.1	30	63.6	35
39.1	26	51.9	22	64.2	82
39.4	48	52.4	58	64.8	47
40.5	36	54.0	21	65.1	50
40.9	26	54.2	16	65.7	77
41.1	24	54.6	18	66.4	92
41.6	31	54.8	53	66.7	57
41.9	33	55.3	19	67.0	6.4
42.5	29	55.6	8.5	67.6	4.4
42.9	16	56.4	11	67.9	4.3
43.5	7.2	56.8	11	68.5	3.4
43.8	3.3	57.0	14	68.9	3.2
44.3	4.2	58.0	22	69.9	3.6
44.9	4.4	58.3	28	70.7	6.2
45.3	11	58.7	17	71.4	21
45.7	13	59.6	31	72.2	20
46.1	14	60.1	25	72.7	29
46.6	22	60.6	23	73.2	29
47.1	69	60.9	31	73.5	39
47.8	38	61.1	16	73.9	54
48.6	64	61.4	18	74.3	24
48.9	65	61.7	31	74.6	20

Table II

Absorption Coefficients of O_2 in the Spectral Region 1075-1100A

λ = wavelength in A

k = absorption coefficient in cm^{-1}

λ	k	λ	k	λ	k
1075.2	8.7	1083.0	51	1091.1	3.0
75.9	5.8	84.1	29	91.8	2.1
76.6	5.8	84.5	59	92.4	2.3
77.0	3.7	85.2	72	92.8	2.7
77.4	12	86.0	16	93.5	2.8
77.7	11	86.3	10	94.0	3.5
78.0	23	86.8	7.3	94.7	1.8
78.4	15	87.1	9.9	96.0	3.5
78.8	21	87.5	21	97.2	7.3
79.7	59	88.6	14	97.6	5.1
81.4	41	89.9	14	98.0	5.7
81.8	62	90.5	11	99.5	6.7
82.3	21				

ACKNOWLEDGEMENTS

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