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Absorption in the spectral range of the Schumann–Runge bands

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Absorption of silicon lines by O_2 in the Schumann–Runge bands has been measured. The results lead to some conclusions about the nature of the absorption and about the general behavior of the spectrum.

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Introduction

Early measurements, presented in Fig. 1, of the absorption coefficient of oxygen in the Schumann–

Runge bands (1750–2000 Å) and in the Herzberg continuum ($\lambda < 2424$ Å) were mainly performed with light sources providing spectral emission
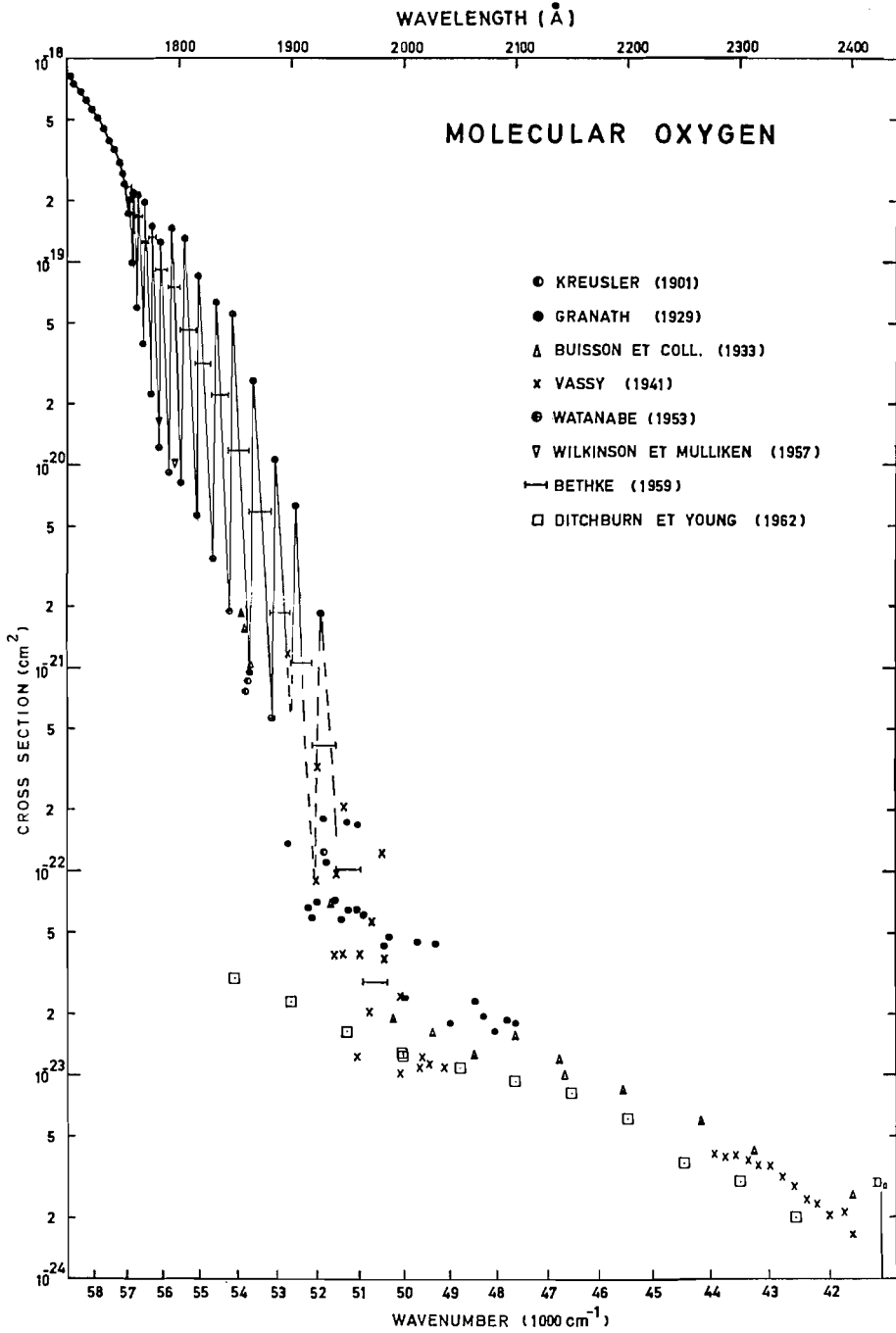
FIG. 1. Absorption cross section of molecular oxygen σ_{O_2} between 1700 and 2430 Å. The uncertainty remaining in the Schumann–Runge bands after measurements extending over a period of more than 60 years appears clearly.

TABLE I

Data

Band	Line	ν_{O_2}(cm⁻¹)	ν_{Si}(cm⁻¹)	$\Delta\nu$(cm⁻¹)	$\overline{\Delta\nu}$(cm⁻¹)	S Bethke (cm)	r_J	$\sigma_{\nu_o}(O_2)$ (cm²)	σ_ν(Si) (cm²)	$\dfrac{\sigma_\nu(Si)}{\Sigma\sigma_o(O_2)}$
5–0	7P	52 513.2	52 502.7	10.5	13.2	6.44×10^{-19}	0.06589	4.24×10^{-20}	5.26×10^{-22}	2.99×10^{-3}
	9R	52 511.9		9.2			0.07434	4.79×10^{-20}		
	9P	52 486.5		16.2			0.06690	4.31×10^{-20}		
	11R	52 485.5		17.2			0.06664	4.29×10^{-20}		
6–0	19P	52 823.3	52 819.2	4.1	3.8	1.53×10^{-18}	0.01186	2.89×10^{-20}	1.31×10^{-21}	2.57×10^{-2}
	21R	52 822.6		3.4			0.01236	1.89×10^{-20}	1.23×10^{-21}	
6–0	13P	52 973.4	52 974.7	1.3	1.3	1.53×10^{-18}	0.05102	7.81×10^{-20}	1.79×10^{-20}	1.20×10^{-1}
	15R						0.04198	6.42×10^{-20}	1.71×10^{-20}	
7–0	25P	53 141.1	53 139.1	2.0	2.5	3.15×10^{-18}	0.00380	1.20×10^{-20}	8.28×10^{-22}	4.49×10^{-2}
	27R	53 135.6		3.5			0.00204	6.43×10^{-21}		
7–0	19P	53 349.1	53 310.2	38.9	33.2	3.15×10^{-18}	0.01886	5.94×10^{-20}	1.50×10^{-22}	1.05×10^{-3}
	21R	53 345.4		35.2			0.01236	3.89×10^{-20}		
	21P	53 285.6		24.6			0.01180	3.72×10^{-20}		
	23R	53 281.4		28.8			0.00722	2.27×10^{-20}		
7–0	19P	53 349.1	53 337.8	11.3	9.8	3.15×10^{-18}	0.01886	5.94×10^{-20}	4.06×10^{-22}	4.35×10^{-3}
	21R	53 345.4		7.6			0.01236	3.89×10^{-20}	4.28×10^{-22}	
7–0	17P	53 406.7	53 387.3	19.4	26.6	3.15×10^{-18}	0.02821	8.89×10^{-20}	3.14×10^{-22}	1.26×10^{-3}
	19R	53 403.6		16.3			0.01986	6.26×10^{-20}		
	19P	53 349.1		38.2			0.01886	5.94×10^{-20}		
	21R	53 345.4		41.9			0.01236	3.89×10^{-20}		
8–0	13P	54 000.4	53 981.9	18.5	22.5	5.98×10^{-18}	0.05102	3.05×10^{-19}	1.19×10^{-21}	1.14×10^{-3}
	15R	53 995.3		13.4			0.04198	2.51×10^{-19}	1.11×10^{-21}	
	15P	53 953.5		28.4			0.03936	2.35×10^{-19}		
	17R	53 947.8		34.1			0.02987	1.79×10^{-19}		
8–0	13R	54 036.8	54 034.4	2.4	2.4	5.98×10^{-18}	0.05494	3.29×10^{-19}	1.40×10^{-20}	3.98×10^{-2}
									1.31×10^{-20}	
8–0	7P	54 104.1	54 090.7	13.4	14.4	5.98×10^{-18}	0.06589	3.94×10^{-19}	2.96×10^{-21}	2.07×10^{-3}
	9R	54 101.5		10.8			0.07434	4.45×10^{-19}	3.39×10^{-21}	
	9P	54 075.6		15.1			0.06690	4.00×10^{-19}		
	11R	54 072.2		18.5			0.06664	3.99×10^{-19}		
8–0	7P	54 104.1	54 108.2	4.1	5.5	5.98×10^{-18}	0.06589	3.94×10^{-19}	6.95×10^{-21}	9.19×10^{-3}
	9R	54 101.5		6.7			0.07434	4.45×10^{-19}	7.71×10^{-21}	
8–0	5P	54 126.7	54 128.0	1.3	2.4	5.98×10^{-18}	0.05637	3.37×10^{-19}	3.20×10^{-20}	4.87×10^{-2}
	7R	54 124.7		3.3			0.07530	4.50×10^{-19}	3.83×10^{-20}	
8–0	1R	54 157.3	54 167.9	10.6	13.4	5.98×10^{-18}	0.02726	1.63×10^{-19}	1.71×10^{-21}	3.01×10^{-3}
	1P	54 152.7		15.2			0.01363	8.15×10^{-20}	1.85×10^{-21}	
	3R						0.05110	3.05×10^{-19}		
9–0	23P	54 158.0		9.9		9.49×10^{-18}	0.00692	6.57×10^{-20}		

Band	Line	ν_{O_2} (cm⁻¹)	ν_{Si} (cm⁻¹)	$\Delta\nu$ (cm⁻¹)	$\overline{\Delta\nu}$ (cm⁻¹)	S Bethke (cm)	r_j	$\sigma_{\nu_0}(O_2)$ (cm²)	$\sigma_\nu(Si)$ (cm²)	$\dfrac{\sigma_\nu(Si)}{\Sigma\sigma_{\nu_0}(O_2)}$
8-0	1R	54 157.3		28.0			0.02726	1.63×10^{-19}		
	1P	54 152.7	54 185.3	32.6	33.2	5.98×10^{-18}	0.01363	8.15×10^{-20}	$(5.50\times10^{-22}$	6.43×10^{-4}
9-0	3R			33.3			0.05110	3.05×10^{-19}	$5.12\times10^{-22})$	
	23R	54 218.6		27.3			0.00722	6.86×10^{-20}		
	23P	54 158.0		46.5				6.57×10^{-20}		
	21P	54 231.8				9.49×10^{-18}	0.01180	1.12×10^{-19}		
9-0	21P	54 231.8	54 236.7	4.9	4.9	9.49×10^{-18}	0.01180	1.12×10^{-19}	$(2.06\times10^{-21}$, 2.11×10^{-21}	1.88×10^{-2}
10-0	29P	54 306.3	54 305.1	1.2	1.2	1.38×10^{-17}	0.00096	1.32×10^{-20}	$(6.57\times10^{-21}$, 7.54×10^{-21}	5.71×10^{-1}
9-0	19P	54 298.1	54 313.8	15.7	15.2	9.49×10^{-18}	0.01886	1.79×10^{-19}	$(2.95\times10^{-22}$, 2.87×10^{-22}	1.49×10^{-3}
10-0	29P	54 306.3		7.5		1.38×10^{-17}	0.00096	1.32×10^{-20}		
9-0	13P	54 462.6	54 451.1	11.5	7.9	9.49×10^{-18}	0.05102	4.85×10^{-19}	$(5.27\times10^{-21}$, 4.24×10^{-21}	4.80×10^{-3}
	15R	54 454.6		3.5			0.04198	3.99×10^{-19}		
10-0	3P	55 037.4	55 038.0	0.6	0.6	1.38×10^{-17}	0.03883	5.29×10^{-19}	1.60×10^{-19}	3.02×10^{-1}
11-0	17P	55 160.2	55 124.4	35.8	32.8	1.91×10^{-17}	0.02821	5.39×10^{-19}	$(1.51\times10^{-21}$, 1.90×10^{-21}	1.25×10^{-3}
	19R	55 142.0		17.6			0.01986	3.79×10^{-19}		
	19P	55 096.1		28.3			0.01886	3.60×10^{-19}		
	21R	55 073.6		50.8			0.01236	2.36×10^{-19}		
11-0	13P	55 270.9	55 276.0	5.1	5.1	1.91×10^{-17}	0.05102	9.74×10^{-19}	1.15×10^{-20}	1.18×10^{-2}
11-0	11P	55 314.8	55 309.4	5.4	6.2	1.91×10^{-17}	0.06109	1.17×10^{-18}	1.21×10^{-20}	5.45×10^{-3}
	13R	55 302.3		7.1			0.05494	1.05×10^{-18}		
14-0	7P$_{2,3}$	55 280.37	56 280.19	0.18	0.18	2.87×10^{-17}	0.04392	1.26×10^{-18}	1.58×10^{-18}	1.25
15-0	9R$_1$	56 465.75	56 467.75	2.01	1.97	2.89×10^{-17}	0.02478	7.14×10^{-19}	4.24×10^{-20}	1.98×10^{-2}
	R$_2$	56 469.41		1.66			0.02478	7.14×10^{-19}		
	R$_3$	56 470.00		2.25			0.02478	7.14×10^{-19}		
15-0	7P$_1$	56 485.54		8.45			0.02196	6.35×10^{-19}		
	P$_2$	56 488.60		11.51			0.02196	6.35×10^{-19}		
	P$_3$	56 488.60		11.51			0.02196	6.35×10^{-19}		
	9R$_1$	56 465.75		11.34			0.02478	7.14×10^{-19}		
	R$_2$	56 469.41	56 477.09	7.68	8.29	2.89×10^{-17}	0.02478	7.14×10^{-19}	1.23×10^{-20}	2.35×10^{-3}
	R$_3$	56 470.00		7.09			0.02478	7.14×10^{-19}		
16-0	15R$_1$	56 472.60		4.49			0.01399	3.90×10^{-19}		
	R$_2$	56 479.69		2.60			0.01399	3.90×10^{-19}		
	R$_3$	56 481.92		4.83			0.01399	3.90×10^{-19}		
16-0	9P$_1$	56 613.38	56 613.79	0.41	0.41	2.80×10^{-17}	0.02230	6.24×10^{-19}	3.46×10^{-19}	5.54×10^{-1}
16-0	9P$_2$	56 617.93	56 623.13	5.20	4.69	2.80×10^{-17}	0.02230	6.24×10^{-19}	2.65×10^{-20}	1.36×10^{-2}
	P$_3$	56 618.84		4.29			0.02230	6.24×10^{-19}		
	R$_1$	56 627.72		4.59			0.02480	6.94×10^{-19}		
16-0	9R$_2$	56 633.90	56 637.28	3.38	3.19	2.80×10^{-17}	0.02478	6.94×10^{-19}	1.42×10^{-19}	7.76×10^{-2}
	R$_3$	56 633.32		3.96			0.02478	6.94×10^{-19}		
17-0	13P$_1$	56 635.58		1.70		2.60×10^{-17}	0.01701	4.42×10^{-19}		
16-0	7P$_2$	56 655.68	56 656.27	0.59	0.59	2.80×10^{-17}	0.02196	6.15×10^{-19}	1.00×10^{-18}	8.13×10^{-1}
	P$_3$	56 655.68					0.02196	6.15×10^{-19}		
16-0	3P$_1$	56 700.37	56 700.25	0.59	0.12	2.80×10^{-17}	0.01278	3.58×10^{-19}	9.25×10^{-19}	1.04
17-0	11P$_2$	56 700.37		0.12		2.60×10^{-17}	0.02036	5.29×10^{-19}		

Note: Values obtained with the 2.17 m length cell are shown in parentheses; others were obtained with the 4.01 m length cell.

lines (1–4). Differences between measured values were not clearly understood before analysis of the rotational structure by Curry and Herzberg (5), Knauss and Ballard (6), and Brix and Herzberg (7), all of whom used continuous light sources and high resolution spectrographs.

Absorption measurements by Watanabe, Inn, and Zelikoff (8) using a hydrogen light source showed an apparent pressure effect due to insufficient resolution. They lead to an order of magnitude of absorption intensity useful for semiquantitative applications. Using a slightly higher resolution and assuming the spectral line width, Ditchburn and Heddle (9) have deduced values of the oscillator strengths of the bands. Such results do not agree with those of Bethke (10), deduced from integrated absorption coefficients measured at high pressure, or with those of Hudson (11), obtained recently at different temperatures. This discrepancy has lead to the conclusion that the line half-widths assumed by Ditchburn and Heddle were too small.

The present article reports measurements of the absorption coefficients of O_2 on more than 30 lines of atomic silicon excited in a microwave discharge tube. Such a light source, already described (12), presents various advantages; the spectral lines are narrow and their wavelengths are known with a high accuracy, the uncertainty being less than 0.0015 Å. In addition, such a source produces practically no continuous radiation.

Experimental

The spectral lines have been isolated in our experiments using a 50 cm focal length vacuum monochromator before entering the absorption cell which was a Pyrex tube closed at each end with a quartz lens. Two cell lengths have been used, 217 and 401 cm. The light intensity was monitored by an E.M.I. 6255 Cd photomultiplier. The output was recorded for various O_2 pressures measured by using mercury manometers and MacLeod gauges.

For the data obtained in the region between the 5–0 and the 17–0 band, Beer's law is obeyed and the values range from 1.5×10^{-22} to 1.6×10^{-18} cm² and are presented in Table I. In a few cases where the wavenumber of an O_2 rotational line differs only by a fraction of a cm⁻¹ from the wavenumber of a silicon line at which the measurement takes place, the absorption cross-section has a negative pressure coefficient. In such cases an inferior limit for the absorption cross-section was obtained by extrapolating to zero pressure. For lower v' values a positive pressure coefficient appears which has already been reported by others (13, 14). We shall not deal here with this part of our data.

Interpretation

The absorption at 56 700.25 cm⁻¹ of one of the Si lines corresponds to the maximum of the $3P_1$ line of the 16.0 band and the $11P_2$ line of the 17.0 band of O_2 which are blended at 56 700.37 cm⁻¹. We infer, from the integrated absorption coefficients given by Bethke and from the relative rotational population, that these lines have an equivalent rectangular width of 1 cm⁻¹.

This value is not in disagreement with those given by Wilkinson and Mulliken (15), Heddle (16), and Hudson (11). Assuming that this value is valid for the bands that we consider here, we have calculated the maxima of absorption cross-section at the center of the lines which are close to the silicon lines. We have then plotted the ratios of the measured values σ to the sum of the maximum values σ_i versus the distance Δv in cm⁻¹, weighted according to the relation

$$\Delta v \, (cm^{-1}) = \frac{\sum \Delta v_i \sigma_i}{\sum \sigma_i}$$

The graph of Fig. 2 shows the absorption dependence of the distance from the line even at 30 cm⁻¹ from the line center. The error bars indicate only the uncertainty on the measured cross-sections. The scattering of the points can be attributed to the uncertainty of the wavenumbers for the bands having v' values lower than 12, to the assumption of a constant half-width and to the overlapping of the bands which affects Bethke's values.

The solid line represents Rice's formula (17) for the shape of a line broadened by predissociation. To obtain the best fit of this curve with our data the half-width has to be fixed at 1.4 cm⁻¹.

Conclusion

A line half-width of 1.4 cm⁻¹, which must be chosen to obtain the best fit to the data mainly at large values of Δv where it has the largest influence on the ratio σ/σ_i, indicates that the band oscillator strengths given by Bethke may be too low by as much as a factor of two or three at least for the v' values smaller than 12.

No continuous absorption underlying the bands on which we report in this article can be deduced from our measurements. The data reported here enforce the old idea of Flory (18)
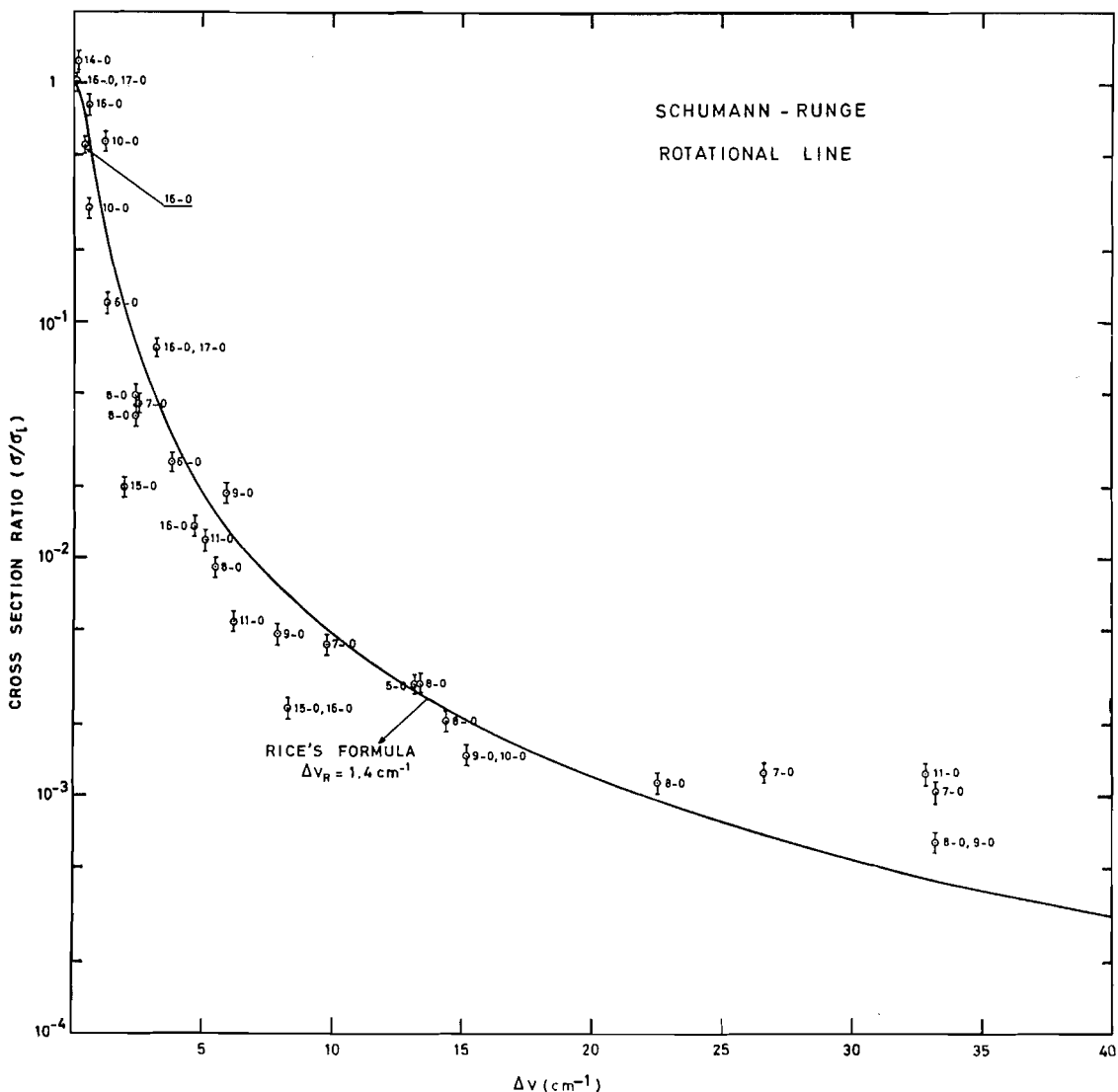
FIG. 2.   Ratios σ/σ_l of the measured cross section σ and calculated cross section at the line center σ_l vs. the distance Δv from the line center.

relating to the predissociation of the oxygen molecule in the Schumann–Runge bands.

A synthetic absorption spectrum can be computed using a line half-width of 1.4 cm^{-1} and Bethke's values for the band oscillator strengths. It exhibits minima and maxima of absorption cross-section which lead to unit optical depth in the atmosphere between altitudes at 25 and 120 km. The deduction of precise values will only become possible when the position of the lines and the strength of the bands has been accurately determined.

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Predissociation in N₂ and O₂[1]

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An outline discussion is given of some of the complications in the measurement of absorption cross sections which arise from finite instrumental bandwidths. Application is made to data on O₂ and N₂ from the literature.

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Introduction

In a recent paper (1) we have shown that published absorption cross sections obtained at maxima or minima could be in error by as much as a factor of two, and that published line and band profiles are probably erroneous because of a failure to take into account the effects of finite instrumental bandwidths. In this paper we should like to present some measurements that we have performed on N₂ (2), and O₂ (3) at high resolution, and to show that another consequence of poor resolution is a loss of information regarding the physical processes that accompany the absorption.

Results

Molecular Oxygen

We would like to discuss the molecular oxygen results first. Our initial aim was to study the effect of temperature on the absorption of oxygen in the Schumann–Runge system, at an instrumental bandwidth of 0.075 Å. The results of our study of the dependence of the continuum on temperature were published some time ago (4). The dependence of the band structure is more complicated as is indicated in Fig. 1, which covers the spectral

range from 1878 to 1894 Å. All three absorption traces were obtained with the same concentration of oxygen in the absorption cell, thus the effects that one sees are due entirely to the redistribution in the ground vibrational and rotational levels. The curve at 600 °K is of special interest as the fraction of molecules in the $v'' = 1$ state at that temperature is 0.0234, and yet the 9–1 band obviously gives rise to more absorption than the 6–0 band. This fact reflects the large increase in Franck–Condon factors from the $v'' = 0$ to the $v'' = 1$ levels due in part to the relatively large (0.4 Å) difference between the internuclear separations of the ground $X^3\Sigma_g^-$ and the excited $B^3\Sigma_u^-$ electronic states. One of the most important findings of the analysis was that all of the upper vibrational levels from $v' = 3$ to 17 were subject to predissociation, the individual rotational lines having half-widths varying from 0.5 to 2.3 cm⁻¹. Predissociation in these bands explains the failure, thus far, to observe fluorescence in the Schumann–Runge bands in the upper atmosphere, and provides an additional source of atomic oxygen between 65 and 95 km, both atoms of which will be left in the ³P state with kinetic energies of up to 1 eV. We have recently measured this photodissociation rate in the laboratory, as a function of column height, at both 200 and 300° K and the resulting atomic oxygen production rate for the CIRA 1965 standard atmosphere (12) is shown in Fig. 2. The curve shown with the Schu-

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