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FOREWORD

This note is the text of a talk given at the "I.A.G.A. Symposium on Laboratory Measurements of Aeronomic Interest", Toronto, September 2, 3 and 4, 1968. It will be published in the Proceedings of the Symposium (Canadian Journal of Chemistry).

AVANT-PROPOS

Cette note constitue le texte d'un exposé fait au "I.A.G.A Symposium on Laboratory Measurements of Aeronomic Interest", Toronto, 2, 3 et 4 septembre 1968. Il sera publié dans les Comptes-Rendus du symposium (Canadian Journal of Chemistry).

VOORWOORD

Deze publicatie bevat de tekst van een toespraak gehouden op het "I.A.G.A. Symposium on Laboratory Measurements of Aeronomic Interest", Toronto, 2, 3 en 4 september 1968. Hij zal verschijnen in het verslag van dit symposium (Canadian Journal of Chemistry).

VORWORT

Diese Notiz ist der Text einer Vorlesung während des "I.A.G.A. Symposium on Laboratory Measurements of Aeronomic Interest", Toronto, 2., 3. und 4. September 1968. Dieser Text wird im Canadian Journal of Chemistry herausgegeben werden.

ABSORPTION IN THE SPECTRAL RANGE OF THE SCHUMANN-RUNGE BANDS

by

M. ACKERMAN, F. BIAUME AND M. NICOLET

Abstract

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.

Résumé

L'absorption de raies du silicium par O_2 dans les bandes de Schumann-Runge a été mesurée. Les résultats permettent de tirer des conclusions sur la nature de l'absorption et sur l'allure générale du spectre.

Samenvatting

De absorptie der siliciumlijnen door O_2 in de Schumann-Runge banden werd gemeten. De resultaten leiden tot gevolgtrekkingen betreffende de aard der absorptie en het algemeen gedrag van het spectrum.

Zusammenfassung

Die Absorption der Siliziumlinien durch O_2 wurde in den Schumann-Runge Banden gemessen. Die Resultaten erlauben Schlussfolgerungen über der Art der Absorption und über dem Allgemeinen Ausschen des Spektrum zu ziehen.

A. INTRODUCTION

Early measurements, presented in figure 1, of the absorption coefficient of oxygen in the Schumann-Runge bands (1750 - 2000 A) and in the Herzberg continuum (λ > 2424A) were mainly performed with light sources providing spectral emission lines[1,2,3,4]. 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 Heedle 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 A. In addition, such a source produces practically no continuous radiation.

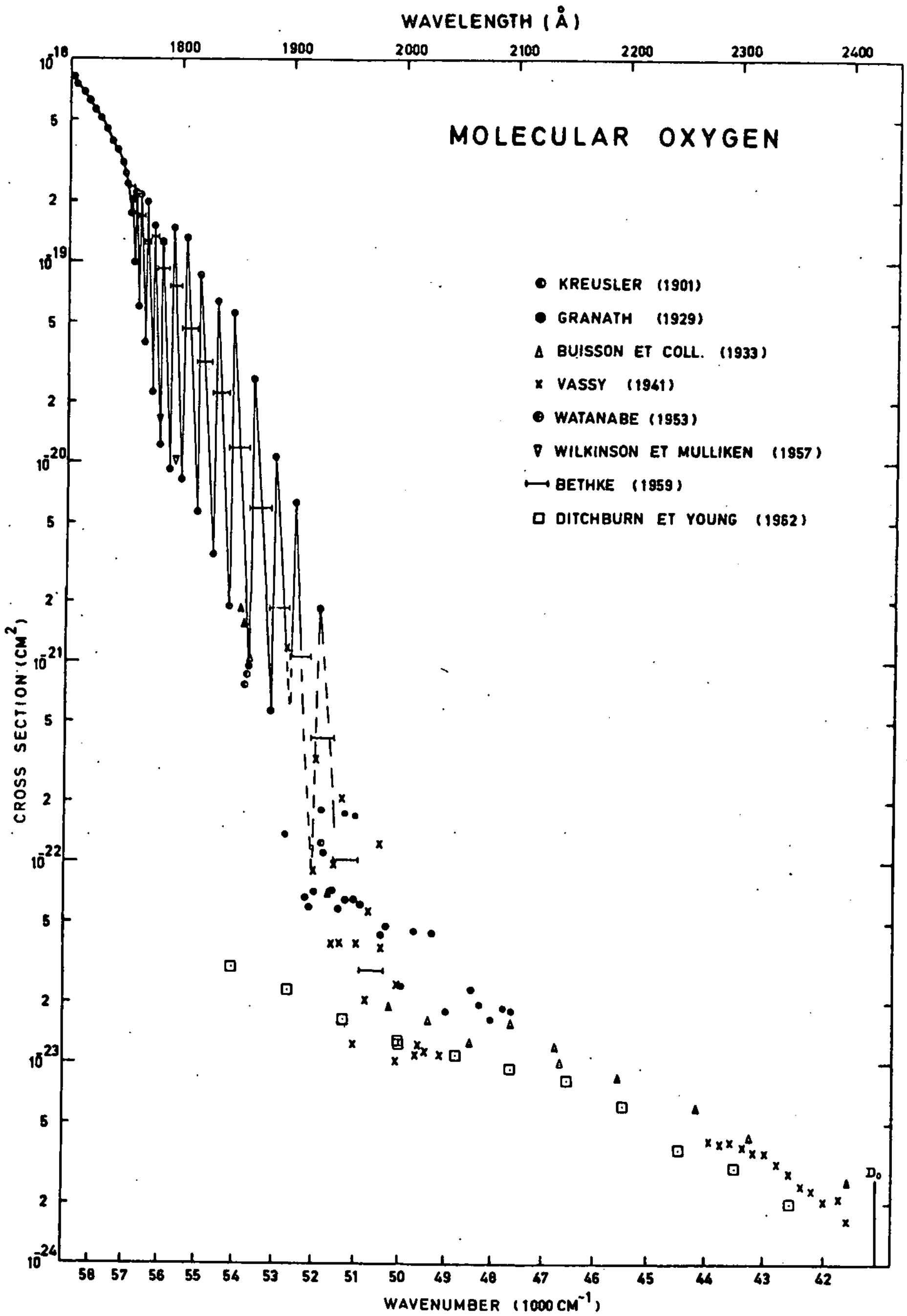

Fig. 1.- Absorption cross section of molecular oxygen σ_{O_2} between 1700 Å and 2430 Å. The uncertainty remaining in the Schumann Runge bands after measurements extending over a period of more than 60 years appears clearly.

B. 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 cm 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 gages.

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} cm^2 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 11 P_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 a equivalent rectangular width of one cm^{-1}.

This value is not in disagreement with those given by Wilkinson and Mulliken[15], Heedle[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 $\Delta\nu$ in cm^{-1}, weighted according to the relation

$$\Delta\nu(cm^{-1}) = \frac{\Sigma\Delta\nu_i\ \sigma_i}{\Sigma\ \sigma_i}$$

The graph of figure 2 shows the absorption dependance 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 so as to obtain the best fit to the date mainly at large values of $\Delta\nu$ where it has the largest influence on the ratio σ/σ_i , indicates that the band oscillator stengths given by Bethke may be to 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] relating to the predissociation of the oxygen molecule in the Schumann Runge bands.

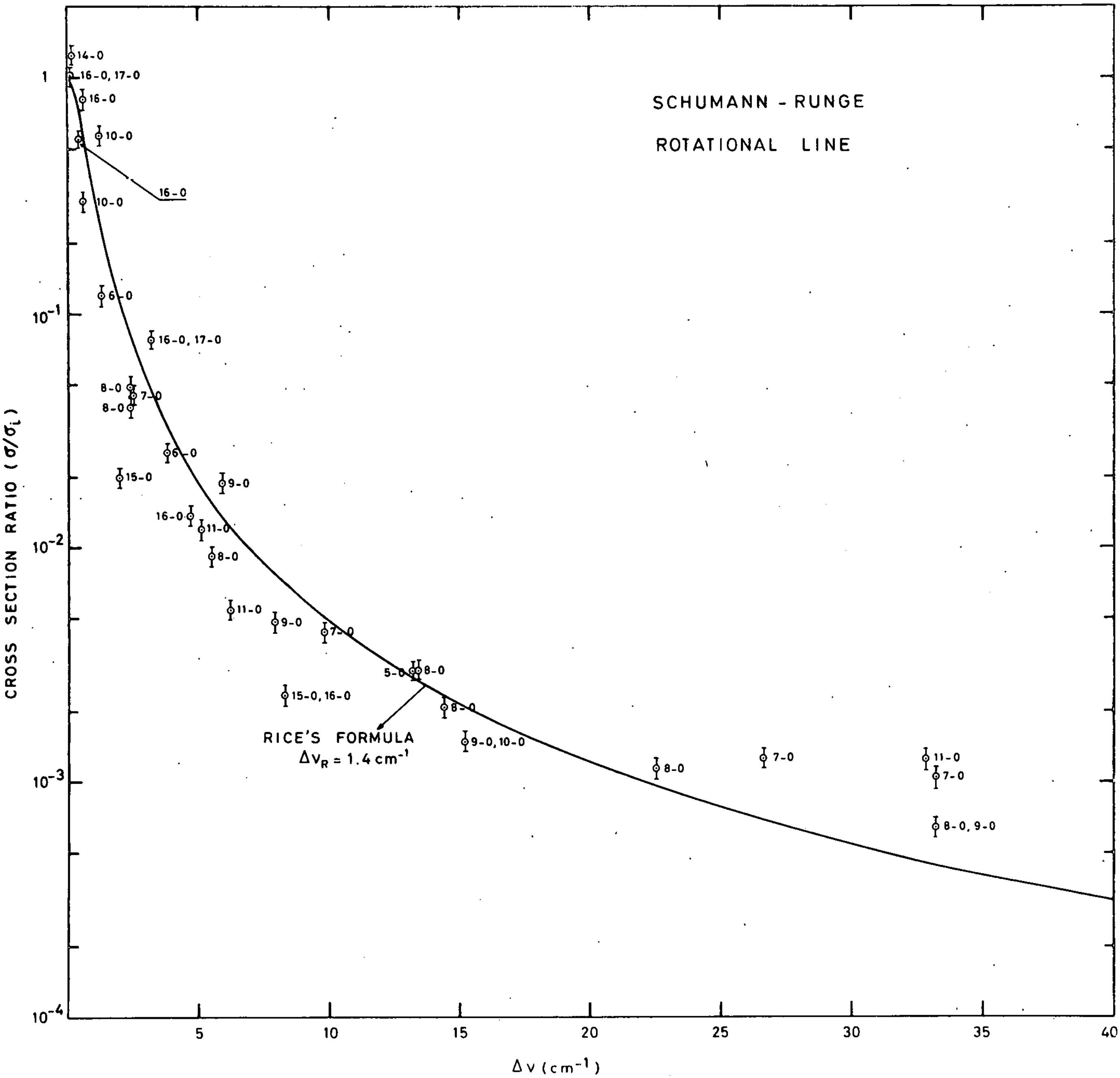

Fig. 2.- Ratios σ/σ_i of the measured cross section σ and calculated cross section at the line center σ_i versus the distance $\Delta\nu$ from the line center.

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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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	σ_ν (O_2) (cm^2)	σ_ν (Si) (cm^2)	$\frac{\sigma_\nu(Si)}{\Sigma\sigma_{\nu_o}(O_2)}$
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}	0.01886	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}		

TABLE I : Data (contd 1)

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	$\sigma_\nu (O_2)$ (cm^2)	$\sigma_\nu (Si)$ (cm^2)	$\frac{\sigma_\nu(Si)}{\Sigma\sigma_{\nu_o}(O_2)}$
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}) 1.11×10^{-21}	1.14×10^{-3}
	15R	53,995.3		13.4			0.04198	2.51×10^{-19}		
	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}) 1.31×10^{-20}	3.98×10^{-2}
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^{-20}) 3.39×10^{-21}	2.07×10^{-3}
	9R	54,101.5		10.8			0.07434	4.45×10^{-19}		
	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}) 7.71×10^{-21}	9.19×10^{-3}
	9R	54,101.5		6.7			0.07434	4.45×10^{-19}		
8-0	5P	54,125.7	54,128.0	1.3	2.4	5.98×10^{-18}	0.05637	3.37×10^{-19}	(3.20×10^{-20}) 3.83×10^{-20})	4.87×10^{-2}
	7R	54,124.7		3.3			0.07530	4.50×10^{-19}		
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}) 1.85×10^{-21}	3.01×10^{-3}
	1P, 3R	54,152.7		15.2			0.01363	8.15×10^{-20}		
							0.05110	3.05×10^{-19}		
9-0	23P	54,158.0		9.9		9.49×10^{-18}	0.00692	6.57×10^{-20}		

TABLE I : Data (contd 2)

Band	Line	ν_{O_2} (cm^{-1})	ν_{Si} (cm^{-1})	$\Delta\nu$ (cm^{-1})	$\overline{\Delta\nu}$ (cm^{-1})	S Bethke (cm)	τ_j	$\sigma_{\nu_o}(O_2)$ (cm^2)	σ_ν(Si) (cm^2)	$\frac{\sigma_\nu(Si)}{\Sigma\sigma_{\nu_o}(O_2)}$
8-0	1R	54,157.3		28.0			0.02726	$1.63x10^{-19}$		
	1P }	54,152.7		32.6		$5.98x10^{-18}$	0.01363	$8.15x10^{-20}$	($5.50x10^{-22}$)	
	3R }		54,185.3		33.2		0.05110	$3.05x10^{-19}$		$6.43x10^{-4}$
9-0	23R	54,218.6		33.3			0.00722	$6.86x10^{-20}$	$5.12x10^{-22}$	
	23P	54,158.0		27.3		$9.49x10^{-18}$	0.00692	$6.57x10^{-20}$		
	21P	54,231.8		46.5			0.01180	$1.12x10^{-19}$		
9-0	21P	54,231.8	54,236.7	4.9	4.9	$9.49x10^{-18}$	0.01180	$1.12x10^{-19}$	($2.06x10^{-21}$) $2.11x10^{-21}$	$1.88x10^{-2}$
10-0	29P	54,306.3	54,305.1	1.2	1.2	$1.38x10^{-17}$	0.00096	$1.32x10^{-20}$	($6.57x10^{-21}$) $7.54x10^{-21}$	$5.71x10^{-1}$
9-0	19P	54,298.1	54,313.8	15.7	15.2	$9.49x10^{-18}$	0.01886	$1.79x10^{-19}$	($2.95x10^{-22}$)	$1.49x10^{-3}$
10-0	29P	54,306.3		7.5		$1.38x10^{-17}$	0.00096	$1.32x10^{-20}$	$2.87x10^{-22}$	
9-0	13P	54,462.6	54,451.1	11.5	7.9	$9.49x10^{-18}$	0.05102	$4.85x10^{-19}$	($5.27x10^{-21}$)	$4.80x10^{-3}$
	15R	54,454.6		3.5			0.04198	$3.99x10^{-19}$	$4.24x10^{-21}$	
10-0	3P	55,037.4	55,038.0	0.6	0.6	$1.38x10^{-17}$	0.03883	$5.29x10^{-19}$	$1.60x10^{-19}$	$3.02x10^{-1}$
11-0	17P	55,160.2	55,124.4	35.8	32.8	$1.91x10^{-17}$	0.02821	$5.39x10^{-19}$	($1.51x10^{-21}$)	$1.25x10^{-3}$
	19R	55,142.0		17.6			0.01986	$3.79x10^{-19}$	$1.90x10^{-21}$	
	19P	55,096.1		28.3			0.01886	$3.60x10^{-19}$		
	21R	55,073.6		50.8			0.01236	$2.36x10^{-19}$		
11-0	13P	55,270.9	55,276.0	5.1	5.1	$1.91x10^{-17}$	0.05102	$9.74x10^{-19}$	$1.15x10^{-20}$	$1.18x10^{-2}$
11-0	11P	55,314.8	55,309.4	5.4	6.2	$1.91x10^{-17}$	0.06109	$1.17x10^{-18}$	$1.21x10^{-20}$	$5.45x10^{-3}$
	13R	55,302.3		7.1			0.05494	$1.05x10^{-18}$		
14-0	$7P_{2,3}$	55,280.37	56,280.19	0.18	0.18	$2.87x10^{-17}$	0.04392	$1.26x10^{-18}$	$1.58x10^{-18}$	1.25

TABLE I : Data (contd 3)

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	$\sigma_{\nu_o}(O_2)$ (cm^2)	$\sigma_\nu(Si)$ (cm^2)	$\frac{\sigma_\nu(Si)}{\Sigma\sigma_{\nu_o}(O_2)}$
15-0	9R$_1$	56,465.75		2.01			0.02478	7.14x10^{-19}		
	R$_2$	56,469.41	56,467.75	1.66	1.97	2.89x10^{-17}	0.02478	7.14x10^{-19}	4.24x10^{-20}	1.98x10^{-2}
	R$_3$	56,470.00		2.25			0.02478	7.14x10^{-19}		
15-0	7P$_1$	56,485.54		8.45			0.02196	6.35x10^{-19}		
	P$_2$	56,488.60		11.51			0.02196	6.35x10^{-19}		
	P$_3$	56,488.60		11.51		2.89x10^{-17}	0.02196	6.35x10^{-19}		
	9R$_1$	56,465.75		11.34			0.02478	7.14x10^{-19}		
	R$_2$	56,469.41	56,477.09	7.68	8.29		0.02478	7.14x10^{-19}	1.23x10^{-20}	2.35x10^{-3}
	R$_3$	56,470.00		7.09			0.02478	7.14x10^{-19}		
16-0	15R$_1$	56,472.60		4.49			0.01399	3.90x10^{-19}		
	R$_2$	56,473.69		2.60		2.80x10^{-17}	0.01399	3.90x10^{-19}		
	R$_3$	56,481.92		4.83			0.01399	3.90x10^{-19}		
16-0	9P$_1$	56,613.38	56,613.79	0.41	0.41	2.80x10^{-17}	0.02230	6.24x10^{-19}	3.46x10^{-19}	5.54x10^{-1}
16-0	9P$_2$	56,617.93		5.20			0.02230	6.24x10^{-19}		
	P$_3$	56,618.84	56,623.13	4.29	4.69	2.80x10^{-17}	0.02230	6.24x10^{-19}	2.65x10^{-20}	1.36x10^{-2}
	R$_1$	56,627.72		4.59			0.02480	6.94x10^{-19}		
16-0	9R$_2$	56,633.90		3.38		2.80x10^{-17}	0.02478	6.94x10^{-19}		
	R$_3$	56,633.32	56,637.28	3.96	3.19		0.02478	6.94x10^{-19}	1.42x10^{-19}	7.76x10^{-2}
17-0	13P$_1$	56,635.58		1.70		2.60x10^{-17}	0.01701	4.42x10^{-19}		

TABLE I : Data (contd 4)

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	$\sigma_{\nu_o}(O_2)$ (cm^2)	$\sigma_\nu(Si)$ (cm^2)	$\frac{\sigma_\nu(Si)}{\Sigma\sigma_{\nu_o}(O_2)}$
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	0.12	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				2.60×10^{-17}	0.02036	5.29×10^{-19}		

Values obtained with the 2.17 meters length cell are shown in parenthesis, others were obtained with the 4.01 meters length cell.