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DETERMINATION OF SPECTROSCOPIC PROPERTIES OF ATMOSPHERIC MOLECULES FROM HIGH RESOLUTION VACUUM ULTRAVIOLET CROSS SECTION AND WAVELENGTH MEASUREMENTS

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Principal Investigator
W.H. Parkinson

Co-Investigators
K. Yoshino
D.E. Freeman

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Greenbelt, Maryland 20771

Smithsonian Institution
Astrophysical Observatory
Cambridge, MA 02138

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The NASA Technical Officer for this grant is Dr. Igor J. Eberstein, Code 616, Goddard Space Flight Center, Greenbelt, Maryland 20771.

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Abstract

An account is given of progress during the six month period 5/1/88-10/31/88 on work on (a) cross section measurements in the transmission window regions of the Schumann-Runge bands of oxygen; (b) the determinations of predissociation linewidths; (c) the theoretical calculation of band oscillator strengths of the Schumann-Runge absorption bands of $^{16}O^{18}O$; (d) the determination of molecular spectroscopic constants; and (e) the combined Herzberg continuum cross sections of ours and those of Reims. The experimental investigations relevant to (a),(b) and (d) are effected at high resolution with a 6.65 m scanning spectrometer which is, by virtue of its small instrumental width (FWHM = 0.0013 nm), uniquely suitable for cross section measurements of molecular bands with discrete rotational structure. Such measurements are needed for accurate calculations of the stratospheric production of atomic oxygen and heavy ozone formed following the photo-predissociation of $^{16}O^{18}O$ by solar radiation penetrating between the absorption lines of $^{16}O_2$.

1. PROGRESS REPORT FOR THE PERIOD 5/1/88-10/31/88

1.1 High Resolution Absorption Cross Section Measurements in the Transmission Window Regions of the Schumann-Runge Bands of Oxygen

For the cross section measurements of the Schumann-Runge bands at room temperature, a 6.65 m scanning spectrometer was used, and its interior served as the absorption cell with an optical pathlength of ~13 m (Yoshino et al. 1983). The oxygen pressure ranged from 0.03 to 80 Torr for measurements of (12,0) - (1,0) bands. The upper limit of 80 Torr of oxygen in the spectrometer was imposed to eliminate the risk of oxidation and combustion of the moving mechanical and electrical components of the photoelectric scanner. Isolation of the scanning compartment from the main tank of the instrument is accomplished by replacing the steel flap valve between the scanning compartment and the main tank with a substitute in which is installed a silica window (Suprasil-2, 30 cm long x 6.4 cm high x 1.3 cm thick) (Cheung et al., 1984; 1986b). With this modification, cross sections as low as 1.0 x 10^{-23} cm^2 are accurately measurable, corresponding to an optical depth, (τ), of 0.3 with 760 Torr of oxygen.

We have completed measurements of the absorption cross sections of the Schumann-Runge bands in the window regions between the rotational lines in the wavelength region 180-195 nm. The measurements have been done with many different pressures of oxygen, 50-760 Torr, so that the pressure dependent absorption can be separated from the main cross sections. Data processing of the cross sections at window regions are in progress.

1.2 The Band Oscillator Strength of the Schumann-Runge Bands of $^{16}O^{18}O$.

The high resolution absorption cross section measurements and band oscillator strengths determinations of the Schumann-Runge bands of $^{16}O^{18}O$ have been completed and a paper submitted for publication to Planetary and Space Science (Yoshino et al., 1989).

1.3 Molecular Spectroscopic Constants of the B $^3\Sigma_u^-$ State of $^{16}O^{18}O$

Spectroscopic constants of the B $^3\Sigma_u^-$ State of $^{16}O^{18}O$ for $2\leq v'\leq 16$ have been determined from the experimental data of line center positions and rotational assignments. The concept of mass-reduced vibrational quantum numbers, $\mu^{-1/2}(v+1/2)$, has been used to combine isotopic molecular constants from $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$. It has been shown that the functions of the vibrational spacings, $\mu^{1/2}\Delta G_{v+1/2}$, rotational constants, μB_v and $\mu^2 D_v$, spin-spin constants, λ_v, and spin-rotation constants, $\mu\gamma_v$, are isotopically invariant functions of $\mu^{-1/2}(v+1/2)$ (see plot of mass-reduced constants μB in Fig. 1).

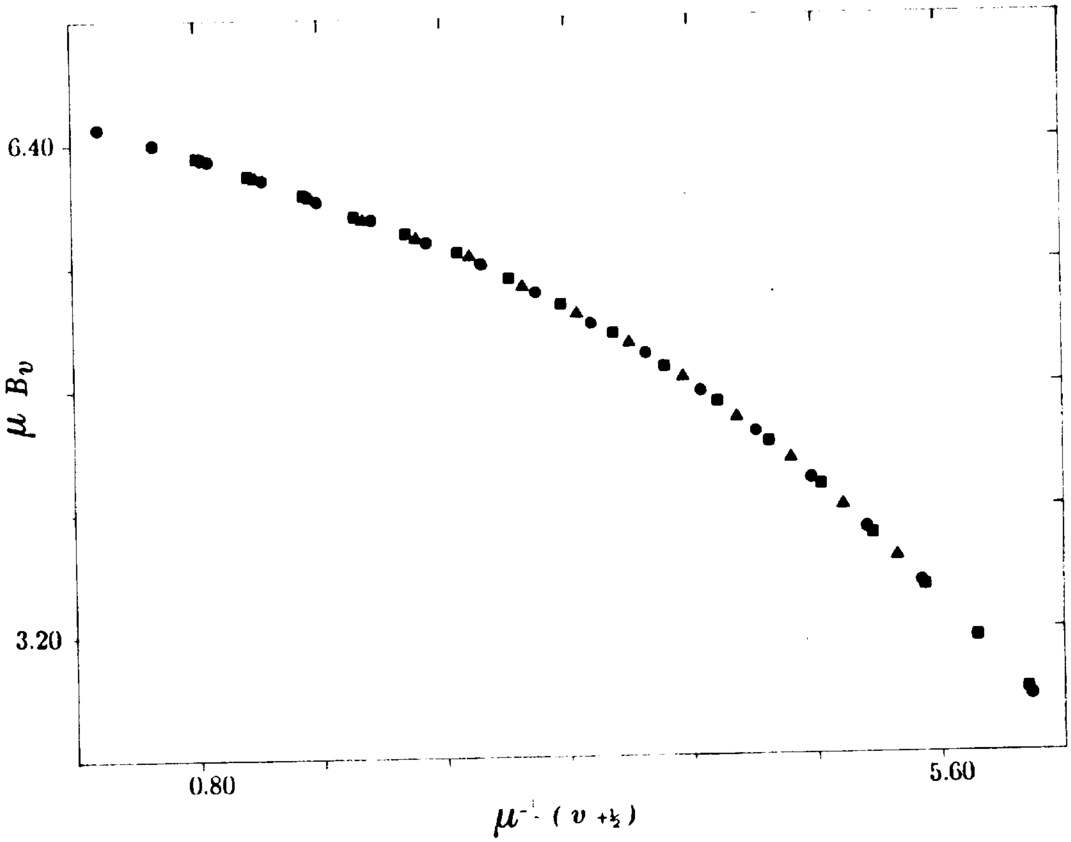

Fig.1 Plot of mass-reduced constants μB

The isotopic dependence of the spin-spin constants λ_v is obtained in terms of the unique perturber approximation. Values of γ_v and λ_v have been obtained by interpolation for the levels v = 2-8, which correspond to bands of $^{16}O^{18}O$ with unresolved triplet structure. In a theoretical investigation, the calculations of level shifts and perturbations have been reexamined. Excellent agreement between calculated and experimental level shifts has been obtained for all three isotopes.

A paper entitled "The Schumann-Runge Absorption Bands of $^{16}O^{18}O$ in the Wavelength Region 175-205 nm and Spectroscopic Constants of Isotopic Oxygen Molecules" has been submitted for publication to the Journal of Molecular Spectroscopy (Cheung et al., 1989).

1.4 Herzberg Continuum Cross Section of Oxygen

A paper entitled "Improved Absorption Cross Sections of Oxygen in the Wavelength Region 205-240 nm of the Herzberg Continuum" has been accepted for publication in Planetary and Space Science (Yoshino et al., 1988).

1.5 Determination of the Predissociation Line Widths of the Schumann-Runge Bands of Oxygen

We developed a computer program that fits, by an interactive non-linear least squares technique, the measured cross section of a complex of overlapping lines by use of a number of Lorentzian components, for which the line center positions and relative line intensities are specified. An initial guessed value of the line width is also input. Previously obtained results for the absorption cross sections (Yoshino et al., 1983) and molecular constants (Cheung et al., 1986a) of the Schumann-Runge bands of $^{16}O_2$ were used as data in the fitting procedure. Because the predissociation widths are large compared with the room temperature Doppler widths, Lorentzian profile were used instead of Voigt profiles. Predissociation line widths of (v',0) band with v'=0-12 are presented in Table 1 for 300K and 79K. The fitting example is shown in Fig. 2 for the band head region of the (11,0) band at 300K and 79K.

Table 1. Predissociation line widths in cm^{-1} of some (v',0) bands with v'=0-12

	(0,0) band 295K		(1,0) band 295K		(2,0) band 295K	
N'	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')
0			1.02		1.05	
2	0.42		1.31	0.82	0.99	1.01
4	0.30		1.21	0.93	1.01	1.05
6	0.30	0.42	0.98	1.01	0.94	0.86
8	0.47	0.39	0.90	1.06	0.88	0.94
10	0.46	0.35	0.90	1.08	0.84	0.85
12	0.45	0.55	0.79	1.09	0.80	0.91
14		0.43	0.76	1.01	0.82	0.83
16		0.49	0.69	0.76	0.84	0.86
18				0.75	0.80	0.88
20				0.64	0.87	0.83
22						0.90

	(3,0) Band				(4,0) Band			
	295K		79K		295K		79K	
N'	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')
0	1.47		1.83		4.21		4.37	
2	1.72	1.47	1.75	1.83	3.66	4.21	3.67	4.37
4	1.76	1.78	1.71	1.85	3.62	4.21	3.89	4.37
6	1.75	1.65	1.77	1.65	3.72	3.66	3.45	3.67
8	1.83	1.92	1.79	1.77	3.67	3.62	3.77	3.89
10	1.73	1.89	1.73	1.82	3.84	3.72	3.93	3.45
12	1.77	1.94		1.90	4.03	3.67		3.77
14	1.80	1.94			3.72	3.77		3.93
16	1.78	1.88			3.95	3.91		
18	1.85	1.72			3.96	3.56		
20		1.92				4.44		
22		1.83						

	(5,0) Band				(6,0) Band			
	295K		79K		295K		79K	
N'	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')
0	2.15		2.22		1.55		1.58	
2	2.10	2.15	2.19	2.22	1.59	1.55	1.66	1.67
4	2.05	2.28	2.15	2.22	1.64	1.69	1.54	1.58
6	2.09	2.10	2.07	2.19	1.69	1.59	1.60	1.66
8	2.08	2.05	2.08	2.15	1.78	1.64	1.71	1.54
10	2.05	2.09	2.13	2.07	1.75	1.69	1.77	1.60
12	2.15	2.08	2.27	2.08	1.88	1.78	1.85	1.71
14	2.08	2.05		2.13	1.93	1.75	1.98	1.77
16	2.07	2.15		2.27	2.06	1.88		1.85
18		2.08			2.17	1.93		1.98
20		2.07			2.30	2.06		
22						2.17		
24						2.30		

	(7,0) Band				(8,0) Band			
	295K		79K		295K		79K	
N'	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')
0	2.02		1.98		1.88		1.79	
2	2.23	2.02	2.18	1.98	1.81	1.88	1.74	1.79
4	1.98	2.02	2.01	1.98	1.81	1.81	1.88	1.74
6	1.98	2.23	1.91	2.18	1.88	1.95	1.82	1.97
8	1.94	1.98	1.86	2.01	2.08	1.87	1.86	1.78
10	1.98	1.98	1.88	1.91	2.01	1.83	1.86	1.81
12	1.92	1.94		1.86	1.95	1.87	1.89	1.80
14	2.19	1.98		1.88	1.97	1.86	2.05	1.92
16	2.09	1.92			1.90	1.99		2.04
18	2.01	2.19			2.15	2.20		2.10
20	2.03	2.09			2.21	2.00		
22		2.01				2.05		
24		2.03				2.04		

	(9,0) Band				(10,0) Band			
	295K		79K		295K		79K	
N'	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')
0	0.95		0.84		1.12		1.23	
2	0.84	0.90	0.80	0.79	1.14	1.19	1.14	1.09
4	0.99	0.95	0.91	0.84	1.11	1.12	1.15	1.23
6	0.96	0.92	0.91	0.92	1.19	1.13	1.09	1.19
8	0.98	0.95	0.88	0.91	1.09	0.99	1.08	1.16
10	0.99	1.01	0.98	0.97	1.10	0.97	0.99	1.08
12	1.06	1.03		0.99	1.01	1.04		1.01
14	1.03	1.02		1.25	1.09	1.12		0.99
16	1.13	1.12			1.06	1.01		
18	1.28	1.37			0.93	1.17		
20	1.44	1.17				1.20		
22		1.24				0.96		

	(11,0) Band				(12,0) Band			
	295K		79K		295K		79K	
N'	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')	P(N')	R(N')
0	1.40		1.43		0.70		0.74	
2	1.30	1.14	1.15	1.23	0.72	0.71	0.76	0.83
4	1.42	1.40	1.37	1.43	0.64	0.80	0.80	0.89
6	1.47	1.49	1.35	1.55	0.85	0.89	0.78	0.90
8	1.42	1.39	1.31	1.52	0.85	0.79	0.78	0.81
10	1.40	1.46	1.46	1.45	0.82	0.87	0.87	0.86
12	1.49	1.48	1.52	1.47	0.88	0.86	0.92	0.95
14	1.54	1.50		1.59	0.98	1.14*		0.96
16	1.60	1.64			0.95	1.00		1.22
18	1.64	1.67				1.05		
20		1.94				1.21		
22		2.07						

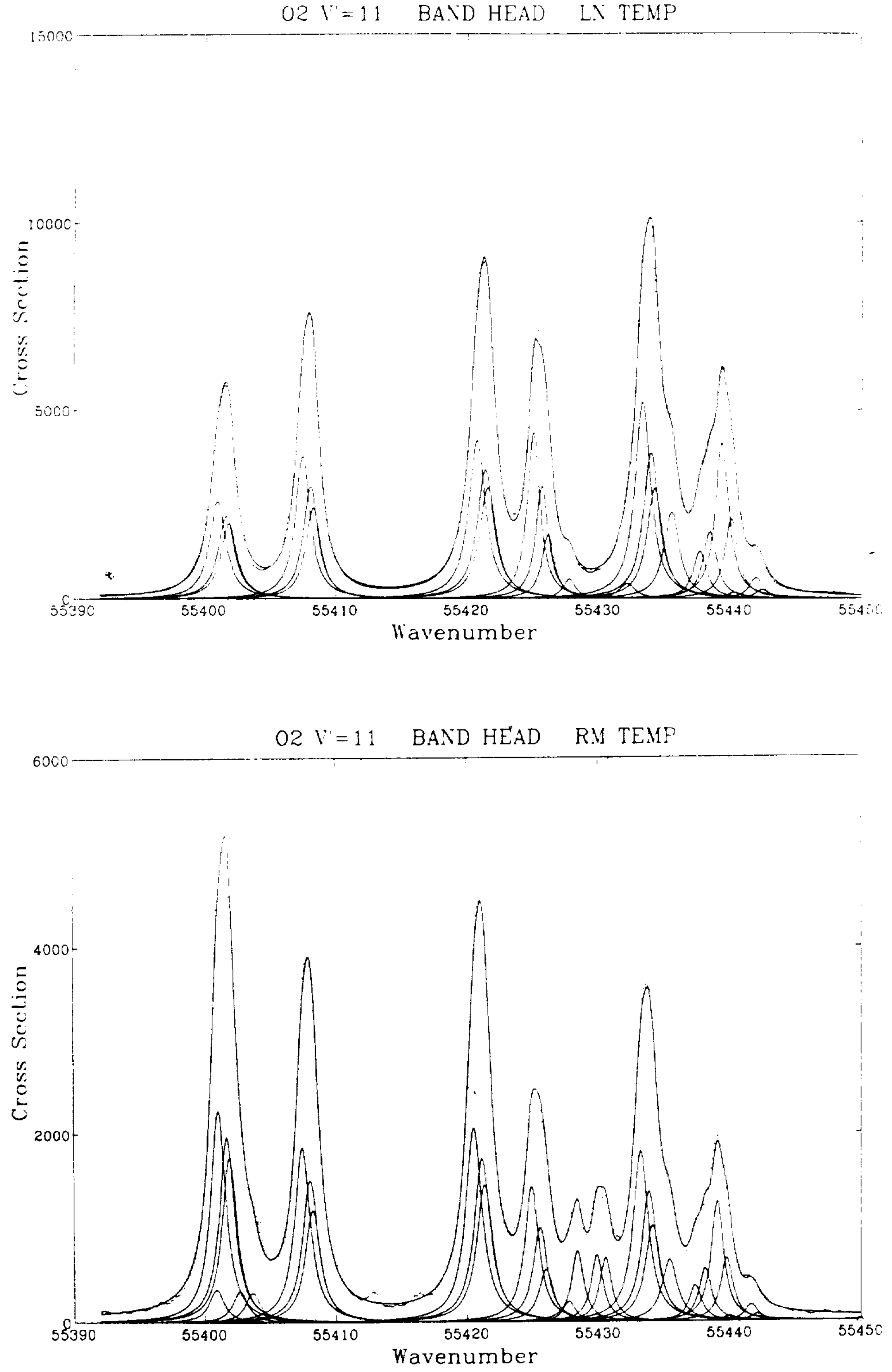

Fig. 2. The line profile fitting of the (11,0) band at 300K and 79K. Small dots are experimental points, and the solid line fitted on the experimental points are the results combined with all components, which are seen as low curves.

2. PUBLICATIONS

2.1 Paper Published and in Press

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2.2 Presentations during the Period 5/1/88 - 10/31/88

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3. REFERENCES

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