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Review

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

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Abstract

An account is given of progress during the six-month period 11/1/92-4/30/93 on work on (a) cross section measurements of the Schumann-Runge continuum; (b) the determination of the predissociation linewidths of the Schumann-Runge bands of O_2; (c) the determination of the molecular constants of the ground state of O_2; (d) cross section measurements of CO_2 in wavelength region 120-170 nm; and (e) determination of dissociation energy of O_2. The experimental investigations 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. Below 175 nm and in the region of the S-R continuum, synchrotron radiation is suitable for cross section measurements. All of these spectroscopic measurements are needed for accurate calculations of the production of atomic oxygen and penetration of solar radiation into the Earth's atmosphere.

1. PROGRESS REPORT FOR THE PERIOD 11/1/92-4/30/93

1.1 Schumann-Runge Continuum Cross Sections of O_2 at 78 K and 295 K.

In the Semiannual Status Report No. 15, we presented the cross sections of the Schumann-Runge continuum at 78 K and 295 K. Cross sections at 295 K were in agreement with previous work within reasonable uncertainties (5~10%), but measurements at 78 K were lower by 20% than those at 295 K over the entire wavelength region. Theoretical calculations of the continuum cross sections indicate only a few percent difference between values at 78 K and 295 K. To clarify this large discrepancy, we have made two additional measurements of the S-R continuum: (1) remeasurements at the Photon Factory with the synchrotron source as background and a 3-m vuv spectrometer, and (2) measurement at the CfA with a C I line as background source and the 6.65-m vuv spectrometer. The results of the new absolute cross sections of the S-R continuum at 78 K and 295 K are listed in Table 1, along with the cross sections at the same wavelength obtained previously from the 1-m instrument. The ratio of cross sections at 78 K and 295 K are almost constants around 0.8 except one at 165.70 nm. The calibrated cross sections from the measurements with the 1-m instrument are presented in Fig. 1 where the absolute cross sections with the 1-m instrument are presented by the open circles and with the 3-m by open triangles. Two crosses in the figure present the results with the 6-m instrument and a C I line source at the CfA. The value at 295 K agrees with the other measurements, but the one at 78 K is only 93% of the value at 295 K (80% for the synchrotron source).

We have no explanation for the low cross section values at 78 K, measured with the synchrotron source as a background. More theoretical studies on the temperature dependency of cross sections of the S-R continuum are in progress. We also plan to experiment with a background source other than the synchrotron. The synchrotron source differs from other sources only by polarization, but we are unable to explain the difference in the cross sections at 78 K.

1.2 Determination of the Predissociation Linewidths of the Schumann-Runge Bands of Oxygen

We reported a single set of parameters characterizing the repulsive potentials of the states that interact with the $B\ ^3\Sigma_u^-$ state through spin-obit coupling and we described the calculation of the predissociation linewidths for various levels with N=0 (Chiu *et al.*, 1992). Here we have calculated the predissociation linewidths in the $B\ ^3\Sigma_u^-$ state with rotational quantum number $N \leq 20$ accounting for the spin-orbit interactions with the $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$ and $^1\Pi_u$ states, and the rotational coupling with the $^3\Pi_u$ state.

Table 1. The absolute cross section measurements of the Schumann-Runge continuum at fixed wavelengths. Previous measurements are listed below each new value.

WL nm	WN cm^{-1}	x	σ_{LN} 10^{-x}	σ_{RT} 10^{-x}	σ_{LN}/σ_{RT}
129.62	77149.	19	4.29	5.11	0.840
131.58	75992.	19	5.35	6.85	0.781
			6.43	7.36	0.874
133.52	74896.	18	1.89	2.26	0.836
			1.963	2.23	0.880
135.47	73818.	18	5.87	7.05	0.833
			6.02	7.20	0.836
138.39	72259.	17	1.099	1.342	0.819
			1.144	1.391	0.822
143.26	69801.	17	1.145	1.420	0.806
			1.172	1.422	0.824
148.14	67504.	17	1.015	1.252	0.811
			1.033	1.269	0.814
153.01	65354.	18	7.47	9.34	0.800
			7.55	9.17	0.823
157.89	63335.	18	4.66	5.76	0.809
			4.61	5.76	0.800
162.77	61437.	18	2.39	2.98	0.802
			2.39	2.97	0.805
165.70	60350.0	18	1.726	1.857	0.929
			1.427	1.828	0.781
167.65	59648.	18	1.032	1.297	0.796
			0.976	1.283	0.761
172.53	57961.	19	3.65	4.63	0.788
			3.53	4.54	0.778

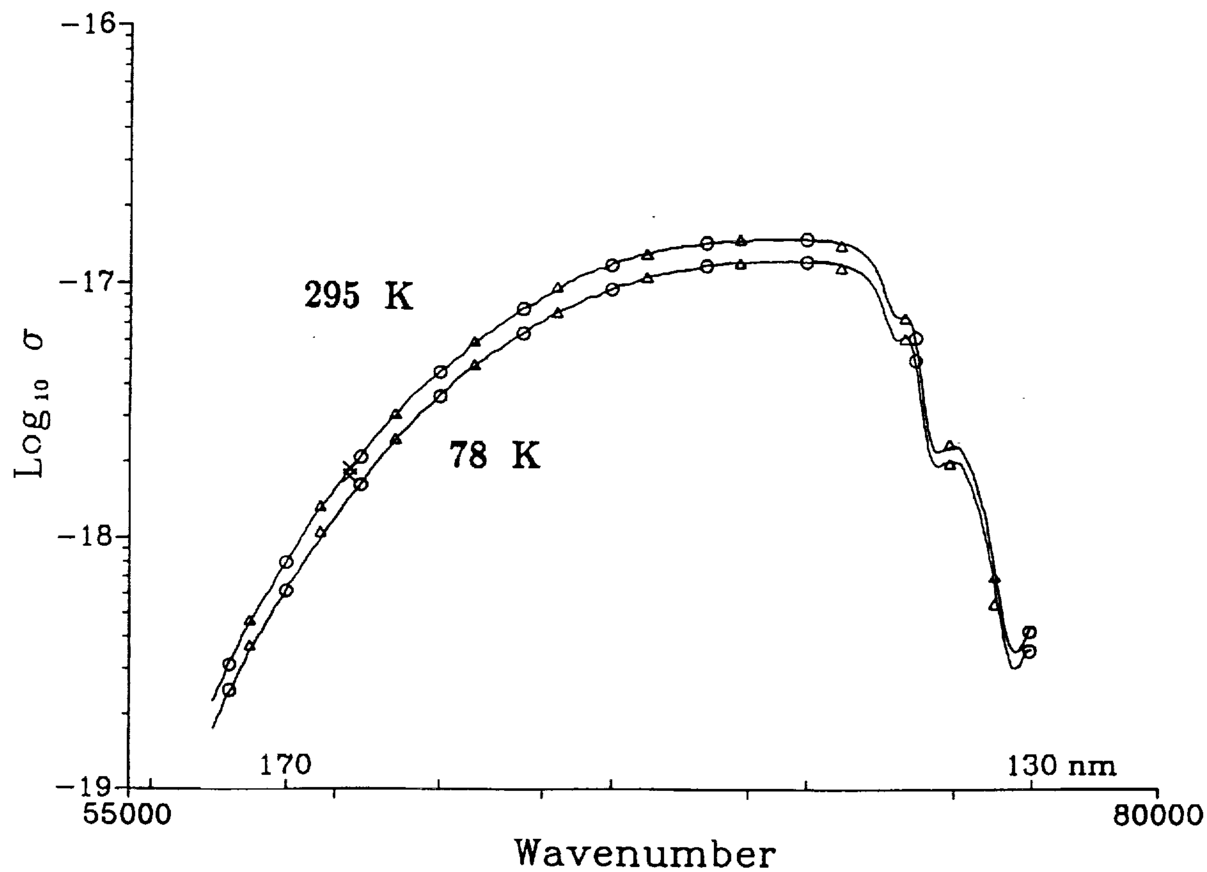

FIG. 1. The cross section of the Schumann-Runge continuum at 78 K and 295 K. Open circles represent the absolute cross sections measured previously to calibrate the relative measurements. Open triangles represent the new absolute cross sections which agree well with the previous values.

Cosby *et al.* (1993) measured the linewidths of each fine structure component for v=0 and 2 using laser-induced, fluorescence spectroscopy. Their averaged linewidths for v=2 and N=0 is smaller than our observed value (Cheung *et al.*, 1990). Our predicted linewidths (Chiu *et al.*, 1992) are larger than the new measurements (Cosby *et al.*, 1993) for v=0 and smaller for v=2. These differences suggest that some modifications are needed in the repulsive potential energy curves and in the interaction strengths. Such alternative set of parameters for the $^1\Pi_u$ state greatly improved the agreement between theory and the new experimental results for v=0 and 2, but yielded poorer agreement with the high v levels. A paper titled "Rotational Dependence of Predissociation Linewidths of the Schumann-Runge Bands of Oxygen" was accepted for publication in Journal of Chemical Physics.

1.3 Molecular Constants for the Ground State, $X\ ^3\Sigma_g^-$, of O_2

The absorption spectrum of O_2 at the high temperature has been photographed with the 6-m vacuum spectrograph at the CfA. Oxygen gas was contained in a heated pipe at 400°C, 210°C, and 150°C in the pressure range 5-400 Torr. The absorption spectrum of the hot Schumann-Runge bands covers the wavelength region 179-211 nm. The absorption lines were measured against a calibration spectrum of the emission bands of CO photographed in the same order. The assignments of the absorption lines of the hot O_2 bands are almost completed. Table 2 presents the rotational assignments of the $B(15)$-$X(3)$ and $B(14)$-$X(3)$ bands from measurements at 400°C.

We had used the rotational term values of the ground state of O_2 by Veseth and Lofthus (1974), however, recent measurements by Rouillé *et al.* (1992) present slightly different values and these differences are large enough to be noticed at our resolution. We will obtain rotational term values of $B(v)$ levels from the new ground levels of v=0 and 1 and our observed absorption bands. After the term values of $B(v)$ levels are settled, we will calculate the term values of the excited ground levels.

Table 2. Wavenumbers of the $B(14)$-$X(3)$ and $B(15)$-$X(3)$ Bands of O_2.

15-3 Band

N	$R_1(N)$	$R_2(N)$	$R_3(N)$	$R_1(N)$	$R_2(N)$	$R_3(N)$
1	51945.87B			51948.85B		
3	51941.08	51944.17B	51944.17B	51934.95	51937.70	51938.24B
5	51925.41	51928.38B	51928.38B	51916.03	51919.01B	51919.01B
7				51889.36	51892.23B	51892.23B
9	51871.15			51854.91B		51858.52B
11	51832.31			51812.81	51816.37	51817.02
13	51785.75	51790.50	51791.31	51762.87	51766.65B	51767.63
15	51731.33	51736.30B	51737.49	51705.23	51709.49B	51710.77
17	51669.09B	51674.04	51676.08	51639.79B	51644.33	51645.99
19	51598.72	51604.21	51606.72	51566.39	51571.39	51573.78B
21	51520.20	51526.39	51529.08H	51485.05B	51490.53B	51492.91
23	51433.84	51440.34	51443.49B	51395.68	51401.65	51404.50B
25	51338.99	51346.09	51350.02	51298.14	51304.65	51308.05
27	51235.76B	51243.11B	51247.96	51192.35	51199.46	51203.00B

14-3 Band

N	$R_1(N)$	$R_2(N)$	$R_3(N)$	$R_1(N)$	$R_2(N)$	$R_3(N)$
1	51739.88					
3	51733.45B	51734.57B	51734.57B	51726.04	51727.76	51728.38
5	51718.16	51720.18B	51720.18B	51707.70	51709.49B	51709.49B
7	51696.29	51698.44	51698.79	51682.03	51683.96B	51684.19
9	51667.03	51669.09B	51669.77B	51649.06	51651.18	51651.49
11	51630.46	51632.98	51633.76	51608.70	51611.01	51611.53
13	51586.45	51589.24	51590.34	51560.99	51563.55B	51564.24
15	51535.03	51538.13B	51539.15	51505.94	51508.70	51509.69
17	51476.12	51479.12B	51481.47B	51443.49B	51446.44B	51447.72
19	51409.66	51413.57B		51373.37	51376.75B	51378.58B
21	51335.49B	51339.49	51341.42	51295.54B	51299.57	51301.29
23	51253.81	51258.13	51260.72B	51210.90	51214.78	51216.82
25	51164.28	51168.97	51171.67	51118.15	51122.43	51124.76
27	51066.88	51072.03	51074.68B	51017.59	51022.32	51024.98

1.4 Cross section measurements of carbon dioxide bands in the region 120-200 nm and their temperature dependence

The absorption spectrum of CO_2 has been photographed with a 10-m, Eagle-mount, vacuum spectrograph at the Meudon Observatory (Cossart-Magos *et al.*, 1992) in the wavelength region 170-200 nm. The entire CO_2 spectrum was kindly supplied for our investigation. These spectra were taken with a resolution of 0.0008 nm for a slit width of 30μm. This is sufficient to judge the resolution necessary for scanning the spectrum with a spectrometer. The absorption spectrum of CO_2 consists of many fine structures above the 175 nm region. Some of the bands have been analyzed by Cossart-Magos *et al.*, (1992). Photoabsorption cross sections of these bands above 175 nm should be measured with a high resolution instrument, but the bands below 175 nm could be done with medium resolution. This was also confirmed with photographs taken at the Photon Factory, KEK, Japan.

The cross sections of CO_2 were measured recently at 195 K and 295 K in the wavelength region 118-178 nm by using the 3-m vuv spectrometer at the Photon Factory, KEK, Japan. The synchrotron source is used as background source. In the scan mode, we covered a 10 nm range by counting at every 0.005 nm. The absolute cross sections were obtained with at least two points in the single scan range. At each such wavelength, we measured signals without CO_2 in the absorption cell, and with CO_2 in it, alternately. The background intensity can be estimated from the average of alternate measurements without CO_2. We used at least six different pressures of CO_2. The absolute cross sections observed at 195 K and 295 K are presented in Table 3. Quite large temperature dependencies were observed. Scanned cross sections are now calibrated on the absolute scale and they are shown in Figs. 2A and 2B for 195 K and 295 K, respectively.

Table 3. Absolute Cross Sections of CO_2 at 195 K and 295 K.

λ_{cal}, nm	WN, cm^{-1}	Temp. K	σ	$\sigma_{195}/\sigma_{295}$
121.356	82402.2	195	$(4.37 \pm 0.06)\times10^{-20}$	0.86
121.357	82401.5	295	$(5.08 \pm 0.09)\times10^{-20}$	
125.583	79628.5	195	$(1.598 \pm 0.022)\times10^{-19}$	0.87
125.585	79627.3	295	$(1.829 \pm 0.024)\times10^{-19}$	
127.626	78354.0	195	$(2.29 \pm 0.02)\times10^{-19}$	0.83
127.626	78354.0	295	$(2.77 \pm 0.04)\times10^{-19}$	
132.069	75718.0	195	$(4.31 \pm 0.05)\times10^{-19}$	0.80
132.029	75740.9	295	$(5.37 \pm 0.10)\times10^{-19}$	
135.516	73792.3	195	$(4.85 \pm 0.03)\times10^{-19}$	0.90
135.564	73765.8	295	$(5.36 \pm 0.05)\times10^{-19}$	
140.600	71123.8	195	$(4.60 \pm 0.04)\times10^{-19}$	0.96
140.602	71122.8	295	$(4.78 \pm 0.12)\times10^{-19}$	
143.866	69509.1	195	$(4.66 \pm 0.05)\times10^{-19}$	0.95
143.869	69507.7	295	$(4.93 \pm 0.06)\times10^{-19}$	
150.030	66653.5	195	$(3.65 \pm 0.06)\times10^{-19}$	0.89
150.010	66662.2	295	$(4.12 \pm 0.04)\times10^{-19}$	
153.727	65050.5	195	$(2.97 \pm 0.03)\times10^{-19}$	0.89
153.707	65057.7	295	$(3.33 \pm 0.04)\times10^{-19}$	
160.789	62193.4	195	$(9.27 \pm 0.03)\times10^{-20}$	0.78
160.789	62193.4	295	$(1.191 \pm 0.019)\times10^{-19}$	
168.977	59179.5	195	$(1.840 \pm 0.045)\times10^{-20}$	0.69
168.978	59179.2	295	$(2.68 \pm 0.04)\times10^{-20}$	
171.907	58170.9	195	$(6.59 \pm 0.07)\times10^{-21}$	0.55
171.907	58170.9	295	$(1.209 \pm 0.084)\times10^{-20}$	

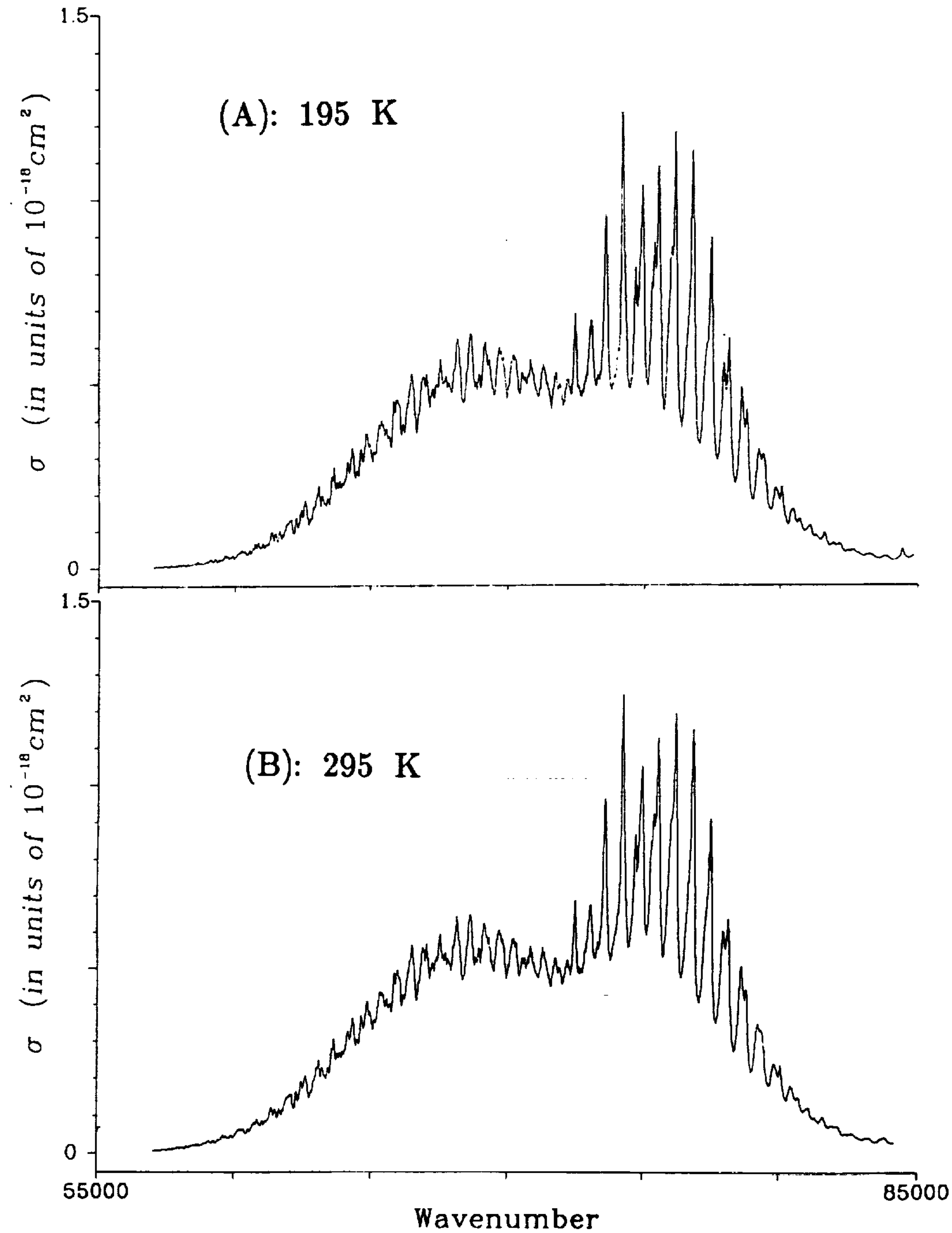

FIG. 2. The cross sections of CO_2 at 195 K and 295K.

Above 170 nm the absorption spectrum of CO_2 begins to show more fine structures which might be lost in a measurement under medium resolution. We will continue to measure cross sections of CO_2 in the wavelength region 170-180 nm with the 6-m spectrometer at the Photon Factory. The cross sections above 180 nm will be measured by the 6-m spectrometer at the CfA.

1.5 Determination of dissociation energy of O_2.

We propose to take photographic absorption spectrum of the Schumann-Runge bands of O_2 near its dissociation limit at SSJ temperature ($\sim$20 K) with an increased resolution of 0.1 cm^{-1} by using a new grating of 4800 l/mm. The gratings have been delivered and tested. The gratings passed tests of focusing properties and of minimum ghosts. However, the gratings appear to be poorly blazed and have low reflecting efficiency above 120 nm.

2. PUBLICATIONS

2.1 Papers Published and in Press (1990-93)

Predissociation Line Widths of the (1,0)-(12,0) Schumann-Runge Absorption Bands of O_2 in the Wavelength Region 179-202 nm, A.S-C. Cheung, K. Yoshino, J.R. Esmond, S.S-L. Chiu, D.E. Freeman and W.H. Parkinson, J. Chem. Phys. **92**, 842-849 (1990).

Predissociation Line Widths of the (3,0)-(11,0) Schumann-Runge Absorption Bands of $^{18}O_2$ and $^{16}O^{18}O$ in the Wavelength Region 180-196 nm, S.S-L. Chiu, A.S-C. Cheung, K. Yoshino, J.R. Esmond, D.E. Freeman and W.H. Parkinson, J. Chem. Phys. **93**, 5539-5543 (1990).

On the Formation of Ozone by Irradiation of Oxygen at 248 Nanometers, D.E. Freeman, K. Yoshino, and W.H. Parkinson, Science, **250**, 1432-1433 (1990).

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Rotational Dependence of Predissociation Linewidths of the Schumann-Runge Bands of Oxygen, A.S-C. Cheung, D.K-W. Mok, M.J. Jamieson, M. Finch, K. Yoshino, A. Dalgarno, and W.H. Parkinson, J. Chem. Phys. accepted for publication.

2.2 Presentations during the period 10/01/92 - 4/30/93

Absorption Cross Section Measurements of the Schumann-Runge Continuum of O_2 at 78 K and 295 K, W.H. Parkinson, J.R. Esmond and K. Yoshino at the 45th Annual Gaseous Electronics Conference, Boston, MA, October 1992.

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