

High resolution absorption cross section measurements of the Schumann-Runge bands of O₂ by VUV Fourier transform spectroscopy

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Introduction

Accurate spectroscopic parameters of the Schumann-Runge (S-R) band system are essential for the current atmospheric photochemical researches. The Harvard-Smithsonian Center for Astrophysics (CfA) group determined the band oscillator strengths for the S-R (1,0) through (12,0) bands directly from the measured cross-section with a resolution of 0.40 cm⁻¹ [1].

In the present study, we report experimental cross-section data at 295 K for the (12,0) through (17,0) bands, in which the linewidths are narrower than 0.4 cm⁻¹. To obtain the spectrum with higher resolution, we used a Fourier transform (FT) spectroscopy for the measurement, with synchrotron radiation light source.

Experimental

FT spectrometer at Imperial College London (IC) [2] was connected to the predisperser system in the beamline 12B. The predisperser system was used to slice a portion of white SR with a bandwidth of 2.5 nm. The diameter of the entrance aperture was set at 1.5 mm. The spectral resolution was either 0.06 or 0.12 cm⁻¹. The absorption cell, with an optical path length of 7.82 cm, was placed between the predisperser and the FT spectrometer, and O₂ gas was introduced at pressures of 2.00, 4.00 and 10.00 Torr at 295 K. For the measurements at 0.12 cm⁻¹ resolution, S/N ratios in the continuum background is about 100 by adding the data of ~400 scans.

Results and Discussion

The observed lines were fitted to the Voigt profiles, using the spectral reduction routine, to obtain accurate line parameters (position, width, intensity).

The unblended strong line positions are in good agreement of <0.1 cm⁻¹, comparing to the measurements by Yoshino *et al.* [3]. The positions of the seriously blended lines could be determined more accurately than previous measurements. The term values and the molecular constants of the B³Σ_u⁻ excited states from v'=12 to 17 were also determined [4].

In Table 1 are listed the band oscillator strengths obtained by the present measurements, together with the previous measurement, Bethke[5], Huebner *et al.* [6], Gies *et al.* [7], Yoshino *et al.* [8], and Lewis *et al.* [9]. The present oscillator strengths are smaller than the other results. In our analysis, the blending between the line of one vibrational band and those of overlapping higher vibrational bands could be separated. It is possible that the blending may have led to overestimates of the band oscillator strengths in the previous measurements.

References

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Table 1: Band oscillator strengths of the Schumann-Runge bands of O₂

Band	Band oscillator strengths (10 ⁻³)					
	Present	Lewis[9]	Yoshino[8]	Gies[7]	Huebner[6]	Bethke[5]
(12,0)	2.38	2.44	2.43	2.74	2.88	2.81
(13,0)	2.62	2.73		2.87	3.41	3.17
(14,0)	2.70	2.82		3.21	3.77	3.24
(15,0)	2.66	2.73		2.95	3.73	3.26
(16,0)	2.40	2.63		2.63	3.53	3.16
(17,0)	2.12			2.64	3.03	2.95