High-resolution photoabsorption cross-section measurements of SO_2 at 160 K between 199 and 220 nm

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[1] Photoabsorption cross sections of sulfur dioxide over a range of temperatures are required to interpret observations and to support models of the atmospheres of Io and Venus. We report high-resolution ($\lambda/\Delta\lambda \approx 450{,}000$) photoabsorption cross-section measurements by Fourier transform spectrometry of SO_2 at 160 K in the wavelength region 199 to 220 nm, which encompasses the strongest features in the prominent $\tilde{C}^1B_2 - \tilde{X}^1A_1$ system. Our results are compared with literature values obtained at lower resolutions and with 295 K cross sections recorded earlier with the same instrument.

1. Introduction

[2] Sulfur dioxide is a significant component of the atmospheres of Io and Venus, and it is observed in the Earth's troposphere and stratosphere following volcanic eruptions. High-resolution photoabsorption cross sections, at relevant temperatures, are required for the reliable interpretation of SO_2 absorption features and for the incorporation of SO_2 in photochemical models of solar system atmospheres including that of the earth. In this paper we report SO_2 photoabsorption cross sections in the 199 to 220 nm region, encompassing the strongest features of the prominent $\tilde{C}^1B_2 - \tilde{X}^1A_1$ system, at 160 K. The measurements, made with a vacuum ultraviolet Fourier transform spectrometer, were performed at a resolving power of $\sim$450,000 ($\Delta\lambda \approx 5.4$ mÅ). The low-temperature measurements are an extension of our ongoing program to survey the SO_2 ultraviolet absorption spectrum at high resolution and a range of temperatures [*Stark et al.*, 1999; *Rufus et al.*, 2003].

[3] *Ballester et al.* [1994] first reported that the ultraviolet albedo of Io is dominated by SO_2 absorption band features; analyses of UV observations from the Hubble Space Telescope [*Clarke et al.*, 1994; *Trafton et al.*, 1996; *Spencer et al.*, 2000; *McGrath et al.*, 2000; *Jessup et al.*, 2004, 2007], the Galileo satellite [*Hendrix et al.*, 1999], and the New Horizons satellite [*Spencer et al.*, 2007] have led to a progressively more refined picture of the spatially variable SO_2 atmospheric distribution. Yet, significant uncertainties remain concerning the atmospheric abundance and spatial distribution of SO_2 on Io, the thermal structure of the atmosphere, and the role of thermal processes involving surface frosts in the formation of the atmosphere [e.g., *Lellouch*, 2005; *Spencer et al.*, 2005; *Moullet et al.*, 2008].

[4] The interpretation of the SO_2 atmospheric features on Io is limited by the lack of high-resolution SO_2 photoabsorption cross-section data at appropriate temperatures. As initially pointed out by *Belton* [1982], saturation of the very sharp SO_2 features may lead to large underestimates of the SO_2 column density when instrumentally broadened absorption spectra are analyzed with low-resolution laboratory-derived cross sections. The direct incorporation of high-resolution laboratory measurements of the SO_2 absorption spectrum that are capable of resolving line profiles is necessary for the further development of atmospheric models of Io. SO_2 temperatures in Io's atmosphere are reported to range roughly from 150 to 250 K [*Jessup et al.*, 2004]. Room temperature cross sections are not sufficient for analyses of Io UV observations, nor can these cross sections be extrapolated to lower temperatures because the energy level structures of the participating electronic states are not well understood.

[5] Sulfur dioxide is also observed in the atmospheres of Venus and Earth. The ground-based observations of *Barker* [1979], leading to the first detection of SO_2 in the atmosphere of Venus, were followed by space-based detections, via UV absorption features, from the Pioneer Venus Orbiter [*Stewart et al.*, 1979; *Esposito et al.*, 1988], the International Ultraviolet Explorer satellite [*Conway et al.*, 1979; *Na et al.*, 1990], the Hubble Space Telescope [*Esposito et al.*, 1997] and sounding rockets [*McClintock et al.*, 1994; *Na et al.*, 1994]. Far more observational data will be available after the anticipated mapping of the vertical SO_2 profile in the Venusian atmosphere by the SPICAV instrument on the ESA Venus Express satellite [*de Bergh et al.*, 2006; J.-L. Bertaux et al., *Temperature structure at Venus as observed by Venus Express* (*SPICAV*), paper presented at 37th Scientific Assembly, Committee on Space Research, Montreal, Quebec, Canada, 2008].

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Table 1. Published SO$_2$ Absorption Data Sets

Reference	Resolving Power	Spectral Range (nm)	Temperatures (K)
Present work	450,000	199–220	160
Danielache et al. [2008]	2000	190–330	293
Wu et al. [2000]	5200	208–295	200, 295, 400
Stark et al. [1999]	450,000	198–220	295
Koplow et al. [1998]	1.5×10^8	215.21–215.23	295
Prahlad and Kumar [1997]	2000	188–220	220–300
Manatt and Lane [1993]	2500	106–403	295
Ahmed and Kumar [1992]	1250	188–231	295
Martinez and Joens [1992]	2200	197–240	295
Freeman et al. [1984]	200,000	172–240	213

[6] Sulfur dioxide in the Earth's atmosphere is observed as a result of volcanic activity [e.g., *Krueger*, 1983; *Eisinger and Burrows*, 1998; *Khokhar et al.*, 2005; *Thomas et al.*, 2005; *Yang et al.*, 2007] and anthropogenic activities [*Wang et al.*, 2006]. Isotopic fractionation in the photodissociation of SO$_2$ by solar radiation in the 180 to 220 nm region has been proposed as the mechanism responsible for the observed non-mass-dependent fractionation in sulfur isotopes in sedimentary sulfates and sulfides [*Farquhar et al.*, 2000, 2001; *Lyons*, 2007]. This geologic sulfur fractionation record is considered to be a prime marker of the rise of oxygen in the Earth's early atmosphere [e.g., *Farquhar et al.*, 2000, 2007; *Pavlov and Kasting*, 2002]. The retrieval of terrestrial SO$_2$ column densities from satellite observations and the quantitative understanding of isotopic fractionation in SO$_2$ atmospheric photodissociation will be furthered by a more complete database of UV SO$_2$ cross sections.

[7] In absorption, the $\tilde{C}^1B_2 - \tilde{X}^1A_1$ electronic system of SO$_2$ comprises a strong series of vibrational bands extending approximately from 170 to 230 nm. The spectrum is complex at room temperature, consisting of densely packed rotational lines within overlapping bands. Vibrational assignments have been made for most of the bands longward of 220 nm [e.g., *Yamanouchi et al.*, 1995] as well as for selected bands at shorter wavelengths [*Okazaki et al.*, 1997]. Rotational assignments are also available for portions of selected bands [*Yamanouchi et al.*, 1995; *Katagiri et al.*, 1997]. The threshold for predissociation of the $\tilde{C}^1B_2$ state was determined by *Becker et al.* [1993, 1995] to be 45,725 cm^{-1}, and the dissociation mechanisms of the $\tilde{C}$ state have been extensively examined [e.g., *Ray et al.*, 1998; *Sako et al.*, 1998; *Okazaki et al.*, 1997; *Cosofret et al.*, 2000; *Hydutsky et al.*, 2008]. Theoretical treatments of the $\tilde{C}$ state using ab initio potential energy surfaces have yielded vibrational energy level predictions and the isotopic variation of vibrational absorption features in the $\tilde{C}^1B_2 - \tilde{X}^1A_1$ system [*Bludsky et al.*, 2000; *Ran et al.*, 2007]. Despite considerable attention, a complete spectroscopic analysis of SO$_2$ absorption in the 180 to 220 nm region has yet to emerge; rotational assignments are not available and vibrational assignments are incomplete, precluding the development of synthetic SO$_2$ spectra or extrapolations of room temperature cross sections to other temperatures.

[8] Previous SO$_2$ cross-section measurements and compilations, encompassing the 199 to 220 nm region, are summarized in Table 1. *Prahlad and Kumar* [1997] and *Wu et al.* [2000], at low resolution, and *Freeman et al.* [1984] report cross sections at temperatures below 295 K. We compare our present results with these literature values in section 3.

2. Experimental Procedure

[9] The SO$_2$ photoabsorption measurements were made using the Imperial College vacuum ultraviolet Fourier transform spectrometer (ICFTS). The ICFTS [*Thorne et al.*, 1987] is capable of recording absorption spectra at resolutions equal to the Doppler widths of individual SO$_2$ lines at 160 K (~2.5 mÅ FWHM at 220 nm). However, predissociation in the $\tilde{C}^1B_2$ state produces broadening in the absorption line profiles, which is noticeable at wavelengths less than ~210 nm, and the highly congested nature of the spectrum results in many multiply blended features with intrinsic widths that are much greater than 2.5 mÅ. A more complete discussion of observed line widths in the $\tilde{C} - \tilde{X}$ system can be found in the work by *Stark et al.* [1999]. Instrumental resolutions (FWHM) of ~5.4 mÅ (0.12 cm^{-1}) and ~7.2 mÅ (0.18 cm^{-1}) were chosen for the 206 to 220 nm and 199 to 206 nm regions, respectively. These instrumental parameters (1) reflect a compromise between resolution and signal-to-noise ratio (SNR) in the time available and (2) replicate the resolutions used in our earlier room temperature cross-section measurements [*Stark et al.*, 1999].

[10] Two continuum light sources were used: a 300 W Hamamatsu xenon arc lamp for wavelengths greater than 215 nm and a 300 W Cathodeon deuterium lamp for $\lambda <$ 215 nm. The continuum radiation was first passed through a zero-deviation, zero-dispersion premonochromator [*Murray*, 1992], with a band pass of ~7 nm, before entering the FT spectrometer. This narrow band pass allowed for the optimization of SO$_2$ column densities in different wavelength regions and reduced the individual integration times needed to record a high S/N absorption spectrum. The spectral ranges of the absorption scans were chosen to produce significant (2 to 3 nm) regions of overlap.

[11] A coolable absorption cell was used to record spectra at a gas temperature of 160 K. The cell consisted of a stainless steel cylinder whose length was adjusted by the positioning of two coaxial cylindrical silica jackets and plastic spacers; a path length of 9.5 cm was used for all measurements. The silica jackets, equipped with quartz windows, were pumpable, allowing an insulating vacuum to be maintained on each side of the gas sample. The entire apparatus was housed in a polystyrene reservoir. Samples of SO$_2$ (B.O.C. 99.9% purity) were used at room temperature pressures ranging from 44.5 mTorr to 79.4 mTorr. All pressures were measured with a 1 Torr capacitance manometer (MKS Baratron). Once filled at room temperature, the absorption cell and a portion of the surrounding gas-handling system were cooled via immersion in a slush of liquid and solid ethanol. The equilibrium between the solid and liquid ethanol produces a constant slush temperature of 159 K [*Lide*, 1994]. Slush temperatures ranging from 159 K to 161 K were measured during the course of spectral scans; we estimate the uncertainty in the stated gas temperature (160 K) of ±1 K. The absorbing SO$_2$ column density was calculated taking into account the volumes of cold (160 K) and warm (295 K) gas in the cell and the gas-handling system. SO$_2$ column densities at 160 K ranged from 1.74×10^{16} to 3.11×10^{16} cm^{-2}.
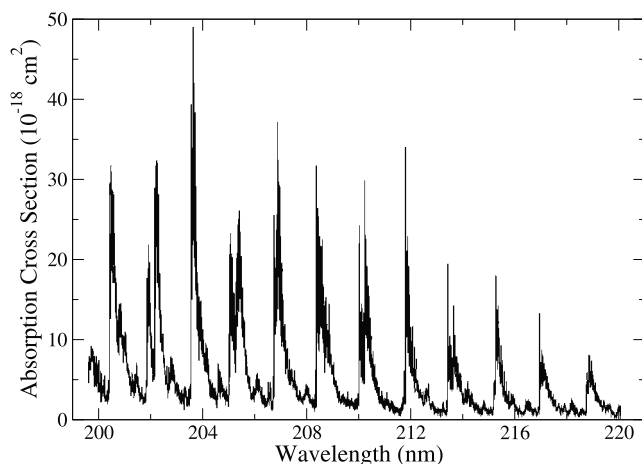
Figure 1. Low-resolution overview of photoabsorption cross sections for SO_2 measured at 160 K. For the purposes of the plot, the cross-section data have been smoothed with a 60 mÅ running average. The displayed peak cross sections are significantly lower than the measured peak cross sections.

[12] The experimental procedure took advantage of the dual output beams of the ICFTS. The absorption cell was positioned in one of the beams while the other beam was used to monitor the intensity of the background continuum, $I_0(v)$. This dual-beam technique allowed $I_0(v)$ to be measured accurately despite the fact that there are no convenient "window" regions of near-zero absorption in the SO_2 spectrum and also compensated for drifts and fluctuations in the intensity of the light source. The two output signals were detected with a pair of solar blind photomultiplier tubes (Hamamatsu R166). To achieve a signal-to-noise ratio of about 70 for the continuum level in the transmission spectra, 320 interferograms, each taking about 100 s to record, were coadded for each 7 nm spectral region. Before and after each set of absorption scans, empty cell values of the two output channel signals were recorded; absolute transmittances were obtained by dividing the full cell ratios by the empty cell ratios. Measurements in all spectral regions were performed at two or more pressures.

3. Results and Analysis

[13] The measured SO_2 absorption spectra were converted to photoabsorption cross sections, $\sigma(v)$, through application of the Beer-Lambert law:

$$\sigma(\nu) = \frac{1}{N} \ln\left[\frac{I_0(\nu)}{I(\nu)}\right], \qquad (1)$$

where N is the SO_2 column density, $I(\nu)$ is the transmitted intensity as a function of wave number through the absorption cell, and $I_o(\nu)$ is the background continuum. Wavelength calibration was achieved via a comparison with precisely measured Fe I and Fe II wavelengths [*Learner and Thorne*, 1988]; we conservatively estimate a 10 mÅ uncertainty in the SO_2 absolute wavelength scale. Figure 1 displays a low-resolution overview of SO_2 cross sections in the 199 to 220 nm region produced by a 60 mÅ running average of the final data set.

[14] The instrumental resolutions of our absorption measurements (~5.4 mÅ and ~7.2 mÅ FWHM) were not sufficient to fully resolve individual SO_2 rotational line profiles when these were Doppler broadened only with widths of 2.5 mÅ FWHM at 160 K. To monitor any optical depth dependence in the measured photoabsorption cross sections associated with inadequate spectral resolution, the 7 nm regions were recorded at multiple pressures. In addition, adjacent pairs of 7 nm regions were spectrally overlapped, allowing for comparisons of derived photoabsorption cross sections at a number of pressures in the overlapping regions. Slight decreases, approximately 10 to 20%, in the measured values of peak cross sections were observed at higher pressures; therefore, the final data set of SO_2 cross sections was compiled from lower pressure scans whenever possible. A series of trial measurements, at somewhat lower spectral resolution, were conducted to verify the stability of the SO_2 sample over extended measurement time periods. Sequential photoabsorption cross-section measurements, on the same static gas sample, produced consistent results in the presence of prolonged irradiation by the UV light source.

[15] Error analysis for FTS absorption spectra is discussed by *Stark et al.* [1999], where it is shown that the fractional statistical uncertainty in the derived SO_2 cross section at any wavelength is

$$\frac{\Delta\sigma}{\sigma} = \left[\left(\frac{\Delta N}{N}\right)^2 + \left(\frac{1}{(SNR)N\sigma}\right)^2 \{1 + e^{2N\sigma}\}\right]^{1/2}. \qquad (2)$$

The two terms in the square root are the fractional uncertainty in the column density (N) and uncertainties associated with the SNR of the measurement and the absorption optical depth ($N\sigma$). The fractional uncertainty in the SO_2 column densities is estimated to be 10%; this relatively large fractional uncertainty stems from uncertainty in the cell temperature and from possible systematic errors in the calculation of the relative quantities of gas in the cold and warm parts of the system. The $N\sigma$ dependence in (2) is such that the second term decreases with increasing $N\sigma$ until the latter is approximately unity. In the targeted range of absorption depths of our measurements, $N\sigma < 0.7$, the estimated total fractional uncertainties in the measured SO_2 cross sections vary from a minimum of approximately 12% in regions of high absorption and large cross section ($\sigma \geq 1 \times 10^{-17}$ cm^2) to as much as 50% in the regions of lowest measurable absorption ($\sigma \leq 2 \times 10^{-18}$ cm^2). This conclusion was confirmed by an examination of regions of spectral overlap between adjacent scans. In regions of high SO_2 cross section, good point-by-point agreement (~10%) was generally found between independent measurements, while significantly larger discrepancies (up to 50%) were observed in multiple scans of regions of low cross section.

[16] A comparison of the present measurements, at 160 K, and the data of *Stark et al.* [1999], which were recorded at equal resolution at 295 K, reveals differences that are clearly attributable to changes in the temperature-dependent rotational population of the ground state. As illustrated in
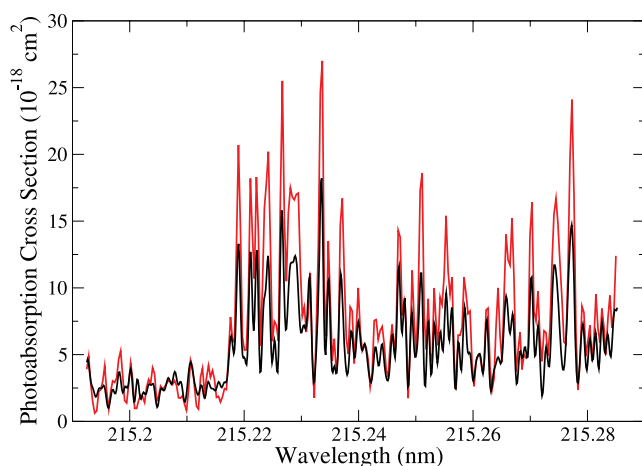
Figure 2. Comparison of 295 K (solid black line) and 160 K (solid red line) measured cross sections in the region of a strong band head (215.22 nm). Low-J rotational levels are more populated at the lower temperature, leading to stronger absorption features in the band head. Both data sets were recorded at a resolution of 5.4 mÅ.

Figure 2, line intensities in the band heads are significantly stronger in the 160 K spectra. While comprehensive rotational assignments are not available for the $\tilde{C} - \tilde{X}$ vibrational bands, the band head spectral regions include transitions from the lowest-J rotational levels of the ground state; these levels have significantly higher populations at the lower temperature. Complementary intensity patterns are seen in spectral regions far from the band heads, presumably the result of decreasing high-J rotational populations at 160 K. However, the congestion of the spectral features and the weakness of many of the lines make these patterns less apparent. At 160 K, approximately 99% of the SO$_2$ molecules are in the (0,0,0) ground vibrational level; at 295 K, about 92% of the molecules remain in the (0,0,0) level, with ~7% being found in the (0,1,0) bending mode. These temperature-dependent changes in the ground state vibrational population are not significant enough to produce noticeable spectral differences in the 295 K and 160 K data sets: no evidence of hot bands is seen in a comparison of the data sets.

[17] The integrated photoabsorption cross section of the 160 K data, over the entire 199 to 220 nm region, is approximately 8% higher than the integrated cross section of the 295 K data. This discrepancy is consistent with our estimations of uncertainties in the two data sets; it may also be caused, in part, by the somewhat arbitrary wavelength interval over which the cross sections are summed: the spectral extent of absorption bands at the edges of the 199 to 220 nm wavelength interval may not be fully measured and their spectral profiles change with temperature. Additionally, integrated cross sections over vibrational bands that terminate on strongly interacting upper state vibrational levels are known to be temperature-dependent [e.g., *Stark et al.*, 2005].

[18] As stated above, spectral patterns associated with hot bands are not observed in a comparison of our 160 K and 295 K data sets. *Wu et al.* [2000], in their low-resolution measurements at 200, 295, and 400 K, over the 208 to 295 nm region, report relatively strong hot bands in the 400 K

spectrum. There is also some indication of hot band-related cross-section differences in their 200 K and 295 K spectra at wavelengths longward of 228 nm (see *Wu et al.* [2000, Figure 2]).

[19] Comparisons of our 160 K data with other published cross sections in the 199 to 220 nm region are complicated by significant differences in spectral resolution. Individual SO$_2$ rotational features are intrinsically narrow; with inadequate instrumental resolution, measured cross sections at the centers of narrow absorption features are consistently underestimated and the cross sections in the "wing" regions between narrow features are consistently overestimated. Integrated cross sections are always underestimated in underresolved measurements. The degree of error is a function of the ratio of line width to instrument profile width, with the largest errors being associated with the lowest resolution. Our instrumental resolutions (this work and *Stark et al.* [1999]), though still underresolving the more weakly predissociated SO$_2$ lines, correspond to a resolving power 2.5 times higher than the best previous broadband measurements [*Freeman et al.*, 1984]. Our measured peak cross sections are as much as a factor of 2 greater than those reported by *Freeman et al.* [1984]. In comparison with all other published measurements (see Table 1), the instrumental resolving power of our FT spectrometer measurements is a factor of 90 or more greater. When compared to two recent low-resolution measurements [*Wu et al.*, 2000; *Danielache et al.*, 2008], our measured peak cross sections in band head regions are typically six to eight times larger. Figure 3 compares the 200 K cross sections of *Wu et al.* [2000], measured with a resolving power of 5200, with our 160 K cross sections over the 210 to 214 nm region.

[20] Our future work on SO$_2$ will extend our low-temperature, high-resolution measurements to the 220 to 325 nm spectral region. This will complete a high-resolution survey, at room temperature [*Stark et al.*, 1999; *Rufus et al.*, 2003] and at cold temperatures, of the 199 to 325 nm region. Numerical tabulations of the SO$_2$ photoabsorption cross sections at 160 K can be obtained from the authors and are also available at http://www.cfa.harvard.edu/amp/ampdata/cfamols.html.
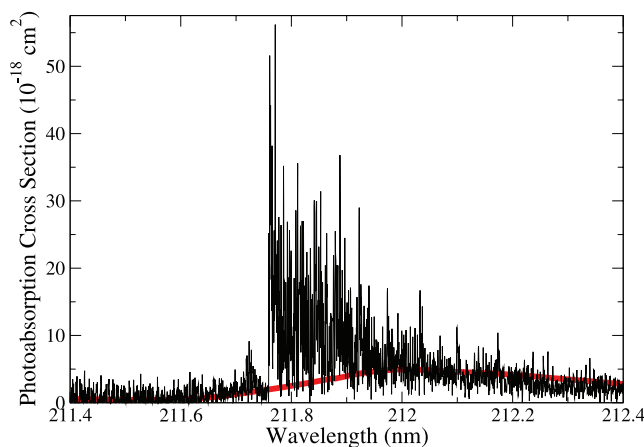

Figure 3. Comparison of our results (solid black line) with the measurements, at 200 K and 400 mÅ resolution, of *Wu et al.* [2000] (solid red line) in the region of the 211.78 nm band head.

References

Ahmed, S. M., and V. Kumar (1992), Quantitative photoabsorption and fluorescence spectroscopy of SO₂ at 188–231 and 278.7–320 nm, *J. Quant. Spectrosc. Radiat. Transfer*, 47, 359–373, doi:10.1016/0022-4073(92)90038-6.

Ballester, G. E., M. A. McGrath, D. F. Strobel, X. Zhu, P. D. Feldman, and H. W. Moos (1994), Detection of the SO₂ atmosphere on Io with the Hubble Space Telescope, *Icarus*, 111, 2–17, doi:10.1006/icar.1994.1129.

Barker, E. S. (1979), Detection of SO₂ in the UV spectrum of Venus, *Geophys. Res. Lett.*, 6, 117–120, doi:10.1029/GL006i002p00117.

Becker, S., C. Braatz, J. Lindner, and E. Tiemann (1993), State specific photodissociation of SO₂ and state selective detection of the SO fragment, *Chem. Phys. Lett.*, 208, 15–20, doi:10.1016/0009-2614(93)80069-2.

Becker, S., C. Braatz, J. Lindner, and E. Tiemann (1995), Investigation of the predissociation of SO₂: State selective detection of the SO and O fragments, *Chem. Phys.*, 196, 275–291, doi:10.1016/0301-0104(95)00114-4.

Belton, M. J. S. (1982), An interpretation of the near-ultraviolet absorption spectrum of SO₂: Implications for Venus, Io, and laboratory measurements, *Icarus*, 52, 149–165, doi:10.1016/0019-1035(82)90175-0.

Bludsky, O., P. Nachtigall, J. Hrusak, and P. Jensen (2000), The calculation of the vibrational states of SO₂ in the $\tilde{C}^1B_2$ electronic state up to the SO($^3\Sigma^-$) + O(^{3}P) dissociation limit, *Chem. Phys. Lett.*, 318, 607–613, doi:10.1016/S0009-2614(00)00015-4.

Clarke, J. T., J. Ajello, J. Luhmann, N. Schneider, and I. Kanik (1994), HST UV spectral observations of Io passing into eclipse, *J. Geophys. Res.*, 99, 8387–8407, doi:10.1029/93JE02547.

Conway, R. R., R. P. McCoy, and C. A. Barth (1979), IUE detection of sulfur dioxide in the atmosphere of Venus, *Geophys. Res. Lett.*, 6, 629–631, doi:10.1029/GL006i007p00629.

Cosofret, B. R., S. M. Dylewski, and P. L. Houston (2000), Changes in the vibrational population of SO $^3\Sigma^-$ from the photodissociation of SO₂ between 202 and 207 nm, *J. Phys. Chem. A*, 104, 10,240–10,246, doi:10.1021/jp001276w.

Danielache, S. O., C. Eskebjerg, M. S. Johnson, Y. Ueno, and N. Yoshida (2008), High precision spectroscopy of ³²S, ³³S and ³⁴S sulfur dioxide: Ultraviolet absorption cross sections and isotope effects, *J. Geophys. Res.*, 113, D17314, doi:10.1029/2007JD009695.

de Bergh, C., V. I. Moroz, F. W. Taylor, D. Crisp, B. Bezard, and L. V. Zasova (2006), The composition of the atmosphere of Venus below 100 km altitude: An overview, *Planet. Space Sci.*, 54, 1389–1397, doi:10.1016/j.pss.2006.04.020.

Eisinger, M., and J. P. Burrows (1998), Tropospheric sulfur dioxide observed by the ERS-2 GOME instrument, *Geophys. Res. Lett.*, 25, 4177–4180, doi:10.1029/1998GL900128.

Esposito, L. W., M. Copley, R. Eckert, L. Gates, A. I. F. Stewart, and H. Worden (1988), Sulfur dioxide at the Venus cloud tops, *J. Geophys. Res.*, 93, 5267–5276, doi:10.1029/JD093iD05p05267.

Esposito, L. W., J.-L. Bertaux, V. Krasnopolsky, V. I. Moroz, and L. V. Zasova (1997), Chemistry of lower atmosphere and clouds, in *Venus-II*, edited by S. W. Bougher et al., pp. 415–458, Univ. of Ariz. Press, Tucson.

Farquhar, J., H. Bao, and M. Thiemens (2000), Atmospheric influence of Earth's earliest sulfur cycle, *Science*, 289, 756–757, doi:10.1126/science.289.5480.756.

Farquhar, J., J. Savarino, S. Airieau, and M. H. Thiemans (2001), Observation of wavelength-sensitive mass-independent sulfur isotope effects during SO₂ photolysis: Implications for the early atmosphere, *J. Geophys. Res.*, 106, 32,829–32,839.

Farquhar, J., M. Peters, D. T. Johnston, H. Strauss, A. Masterson, U. Wiechert, and A. J. Kaufman (2007), Isotopic evidence for Mesoarchaean anoxia and changing atmospheric sulphur chemistry, *Nature*, 449, 706–710, doi:10.1038/nature06202.

Freeman, D. E., K. Yoshino, J. R. Esmond, and W. H. Parkinson (1984), High resolution absorption cross section measurements of SO₂ at 213 K in the wavelength region 172–240 nm, *Planet. Space Sci.*, 32, 1125–1134, doi:10.1016/0032-0633(84)90139-9.

Hendrix, A. R., C. A. Barth, and C. W. Hord (1999), Io's patchy SO₂ atmosphere as measured by the Galileo ultraviolet spectrometer, *J. Geophys. Res.*, 104, 11,817–11,826, doi:10.1029/1999JE900009.

Hydutsky, D. P., N. J. Bianco, and A. W. Castleman (2008), The photodissociation of SO₂ between 200 and 197 nm, *Chem. Phys.*, 350, 212–219, doi:10.1016/j.chemphys.2008.03.001.

Jessup, K. L., J. R. Spencer, G. E. Ballester, R. R. Howell, F. Roesler, M. Vigel, and R. Yelle (2004), The atmospheric signature of Io's Prometheus plume and anti-Jovian hemisphere: Evidence for a sublimation atmosphere, *Icarus*, 169, 197–215, doi:10.1016/j.icarus.2003.11.015.

Jessup, K. L., J. R. Spencer, and R. Yelle (2007), Sulfur volcanism on Io, *Icarus*, 192, 24–40, doi:10.1016/j.icarus.2007.06.025.

Katagiri, H., T. Sako, A. Hishikawa, T. Yazaki, K. Onda, K. Yamanouchi, and K. Yoshino (1997), Experimental and theoretical exploration of photodissociation of SO₂ via the $\tilde{C}^1B_2$ state: Identification of the dissociation pathway, *J. Mol. Struct.*, 413–414, 589–614, doi:10.1016/S0022-2860(97)00199-3.

Khokhar, M. F., C. Frankenberg, M. van Roozendael, S. Beirle, S. Kuhl, A. Richter, U. Platt, and T. Wagner (2005), Satellite observations of atmospheric SO₂ from volcanic eruptions during the time-period of 1996–2002, *Adv. Space Res.*, 36, 879–887, doi:10.1016/j.asr.2005.04.114.

Koplow, J. P., D. A. V. Kliner, and L. Goldberg (1998), Development of a narrow-band, tunable, frequency-quadrupled diode laser for UV absorption spectroscopy, *Appl. Opt.*, 37, 3954–3960, doi:10.1364/AO.37.003954.

Krueger, A. J. (1983), Sighting of El Chichón sulfur dioxide clouds with the Nimbus 7 Total Ozone Mapping Spectrometer, *Science*, 220, 1377–1379, doi:10.1126/science.220.4604.1377.

Learner, R. C. M., and A. P. Thorne (1988), Wavelength calibration of Fourier transform emission spectra with applications to Fe I, *J. Opt. Soc. Am.*, 5, 2045–2059.

Lellouch, E. (2005), Io's atmosphere and surface-atmosphere interactions, *Space Sci. Rev.*, 116, 211–224, doi:10.1007/s11214-005-1957-z.

Lide, D. R. (Ed.) (1994), *CRC Handbook of Chemistry and Physics*, 74th ed., CRC Press, Ann Arbor, Mich.

Lyons, J. R. (2007), Mass-independent fractionation of sulfur isotopes by isotope-selective photodissociation of SO₂, *Geophys. Res. Lett.*, 34, L22811, doi:10.1029/2007GL031031.

Manatt, S. L., and A. L. Lane (1993), A compilation of the absorption cross-sections of SO₂ from 106 to 403 nm, *J. Quant. Spectrosc. Radiat. Transfer*, 50, 267–276, doi:10.1016/0022-4073(93)90077-U.

Martinez, R. D., and J. A. Joens (1992), SO₂ absorption cross section measurements from 197 nm to 240 nm, *Geophys. Res. Lett.*, 19, 277–279, doi:10.1029/91GL03165.

McClintock, W. E., C. A. Barth, and R. A. Kohnert (1994), Sulfur dioxide in the atmosphere of Venus: I. Sounding rocket observations, *Icarus*, 112, 382–388, doi:10.1006/icar.1994.1192.

McGrath, M. A., M. J. S. Belton, J. R. Spencer, and P. Sartoretti (2000), Spatially resolved spectroscopy of Io's Pele plume and SO₂ atmosphere, *Icarus*, 146, 476–493, doi:10.1006/icar.1999.6412.

Moullet, A., E. Lellouch, R. Moreno, M. A. Gurwell, and C. Moore (2008), First disk-resolved millimeter observations of Io's surface and SO₂ atmosphere, *Astron. Astrophys.*, 482, 279–292, doi:10.1051/0004-6361:20078699.

Murray, J. E. (1992), Fourier transform spectrometry of neutral chromium, Ph.D. thesis, Imperial College, London.

Na, C. Y., L. W. Esposito, and T. E. Skinner (1990), International Ultraviolet Explorer observation of Venus SO₂ and SO, *J. Geophys. Res.*, 95, 7485–7491, doi:10.1029/JD095iD06p07485.

Na, C. Y., L. W. Esposito, W. E. McClintock, and C. A. Barth (1994), Sulfur dioxide in the atmosphere of Venus: II. Modeling results, *Icarus*, 112, 389–395, doi:10.1006/icar.1994.1193.

Okazaki, A., T. Ebata, and N. Mikami (1997), Degenerate four-wave mixing and photofragment yield spectroscopic study of jet-cooled SO₂ in the $\tilde{C}^1B_2$ state: Internal conversion followed by dissociation in the X state, *J. Chem. Phys.*, 107, 8752–8758, doi:10.1063/1.475168.

Pavlov, A. A., and J. F. Kasting (2002), Mass-independent fractionation of sulfur isotopes in Archean sediments: Strong evidence for an anoxic Archean atmosphere, *Astrobiology*, 2, 27–41, doi:10.1089/153110702753621321.

Prahlad, V., and V. Kumar (1997), Temperature dependence of photoabsorption cross-sections of sulfur dioxide at 188–220 nm, *J. Quant. Spectrosc. Radiat. Transfer*, 57, 719–723, doi:10.1016/S0022-4073(97)00008-3.

Ran, H., D. Xie, and H. Guo (2007), Theoretical studies of $\tilde{C}^1B_2$ absorption spectra of SO₂ isotopomers, *Chem. Phys. Lett.*, 439, 280–283, doi:10.1016/j.cplett.2007.03.103.

Ray, P. C., M. F. Arendt, and L. J. Butler (1998), Resonance emission spectroscopy of predissociating SO₂ $\tilde{C}$ ($^1B_2$): Coupling with a repulsive $^1A_1$ state near 200 nm, *J. Chem. Phys.*, 109, 5221–5230, doi:10.1063/1.477139.

Rufus, J., G. Stark, P. L. Smith, J. C. Pickering, and A. P. Thorne (2003), High-resolution photoabsorption cross section measurements of SO₂, 2: 220 to 325 nm at 295 K, *J. Geophys. Res.*, 108(E2), 5011, doi:10.1029/2002JE001931.

Sako, T., A. Hishikawa, and K. Yamanouchi (1998), Vibrational propensity in the predissociation rate of SO₂ $\tilde{C}$ ($^1B_2$) by two types of nodal patterns in vibrational wavefunctions, *Chem. Phys. Lett.*, 294, 571–578, doi:10.1016/S0009-2614(98)00922-1.

Spencer, J. R., K. L. Jessup, G. E. Ballester, and R. Yelle (2000), Discovery of gaseous S₂ in Io's Pele plume, *Science*, 288, 1208–1210, doi:10.1126/science.288.5469.1208.

Spencer, J. R., E. Lellouch, M. J. Richter, M. A. López-Valverde, K. L. Jessup, T. K. Greathouse, and J.-M. Flaud (2005), Mid-infrared detection of large longitudinal asymmetries in Io's SO$_2$ atmosphere, *Icarus*, *176*, 283–304, doi:10.1016/j.icarus.2005.01.019.

Spencer, J. R., et al. (2007), Io volcanism seen by New Horizons: A major eruption of the Tvashtar volcano, *Science*, *318*, 240–243, doi:10.1126/science.1147621.

Stark, G., P. L. Smith, J. Rufus, A. P. Thorne, J. C. Pickering, and G. Cox (1999), High-resolution photoabsorption cross-section measurements of SO$_2$ at 295 K between 198 and 220 nm, *J. Geophys. Res.*, *104*, 16,585–16,590, doi:10.1029/1999JE001022.

Stark, G., K. P. Huber, K. Yoshino, P. L. Smith, and K. Ito (2005), Oscillator strength and linewidth measurements of dipole-allowed transitions in ^{14}N$_2$ between 93.5 and 99.5 nm, *J. Chem. Phys.*, *123*, 214303, doi:10.1063/1.2134703.

Stewart, A. I. F., D. E. Anderson, L. W. Esposito, and C. A. Barth (1979), Ultraviolet spectroscopy of Venus: Initial results from the Pioneer Venus Orbiter, *Science*, *203*, 777–778, doi:10.1126/science.203.4382.777.

Thomas, W., T. Erbertseder, T. Ruppert, M. van Roozendael, J. Verdebout, D. Balis, C. Meleti, and C. Zerefos (2005), On the retrieval of volcanic sulfur dioxide emissions from GOME backscatter measurements, *J. Atmos. Chem.*, *50*, 295–320, doi:10.1007/s10874-005-5544-1.

Thorne, A. P., C. J. Harris, I. Wynne-Jones, R. C. M. Learner, and G. Cox (1987), A Fourier transform spectrometer for the vacuum ultraviolet: Design and performance, *J. Phys. E Sci. Instrum.*, *20*, 54–60, doi:10.1088/0022-3735/20/1/010.

Trafton, L. M., J. J. Caldwell, C. Barnet, and C. C. Cunningham (1996), The gaseous sulfur dioxide abundance over Io's leading and trailing hemispheres: HST spectra of Io's $\tilde{C}^1B_2 - \tilde{X}^1A_1$ band of SO$_2$ near 2100 Å, *Astrophys. J.*, *456*, 384–392, doi:10.1086/176660.

Wang, P., A. Richter, M. Bruns, J. P. Burrows, R. Scheele, W. Junkermann, K. P. Heue, T. Wagner, U. Platt, and I. Pundt (2006), Airborne multi-axis DOAS measurements of tropospheric SO$_2$ plumes in the Po-valley, Italy, *Atmos. Chem. Phys.*, *6*, 329–338.

Wu, C. Y. R., B. W. Yang, F. Z. Chen, D. L. Judge, J. Caldwell, and L. M. Trafton (2000), Measurements of high-, room-, and low-temperature photoabsorption cross sections of SO$_2$ in the 2080- to 2950-Å region, with application to Io, *Icarus*, *145*, 289–296, doi:10.1006/icar.1999.6322.

Yamanouchi, K., K. Okunishi, M. Endo, and Y. Tsuchiya (1995), Laser induced fluorescence spectroscopy of the $\tilde{C}^1B_2 - \tilde{X}^1A_1$ band of jet-cooled SO$_2$: Rotational and vibrational analyses in the 235–210 nm region, *J. Mol. Struct.*, *352–353*, 541–559, doi:10.1016/0022-2860(95)08835-J.

Yang, K., N. A. Krotkov, A. J. Krueger, S. A. Carn, P. K. Bhartia, and P. F. Levelt (2007), Retrieval of large volcanic SO$_2$ columns from the Aura Ozone Monitoring Instrument: Comparison and limitations, *J. Geophys. Res.*, *112*, D24S43, doi:10.1029/2007JD008825.

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