Notes

VUV pressure-broadening in sulfur dioxide

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ABSTRACT

In the pre-oxygenated ancient Earth atmosphere, the lack of O_3 absorption allowed ultraviolet photodissociation of numerous molecules in the troposphere and lower stratosphere. For molecules with narrow line-type absorption spectra, optically thick columns would have produced isotope fractionation due to self-shielding of the most abundant isotopologues. In the lower atmosphere pressure broadening would modify, and in some cases, eliminate these isotope signatures. Shielding is particularly important for quantifying or constraining photolysis-derived isotope effects, such as those believed to explain the sulfur mass-independent fractionation in Archean sedimentary rocks. Here, we report pressure broadening coefficients for natural abundance SO_2 in the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ band system at 215 nm. For gas bath pressures up to 750 mbar, we find broadening coefficients of 0.30 ± 0.03 cm^{-1} atm^{-1} and 0.40 ± 0.04 cm^{-1} atm^{-1} for N_2 and CO_2, respectively. These broadening coefficients are ~30% larger than SO_2 broadening coefficients previously measured in the $\tilde{B} - \tilde{X}$ bands at 308 nm. Because of the highly congested nature of the $\tilde{C} - \tilde{X}$ bands, pressure broadening in the early Earth troposphere will cause line profile overlap that will diminish the self-shielding-derived mass-independent isotope fractionation for optically thick SO_2 columns. Thus, non-explosive volcanic eruptions may not have left a signature of SO_2 self-shielding in the ancient sedimentary rock record.

1. Introduction

The discovery of a sulfur isotope mass-independent fractionation (S-MIF) signature in Archean sedimentary rocks [1] has been interpreted as a proxy for the rise of atmospheric O_2. Mass-independent fractionation (MIF) refers to a departure from isotopic equilibrium in geochemical systems containing 3 and 4-isotope elements, such as O and S, respectively. Small MIF signatures are often a result of kinetic effects, but large MIF signatures are usually a result of gas-phase photochemistry, and therefore are most common in atmospheric environments [2,3]. Photolysis of SO_2 has been suggested to be the source of the S-MIF [4–9] with photolysis occurring primarily in the lower stratosphere and troposphere and at wavelengths from ~190 (set by CO_2 absorption) to 219 nm (the SO_2 dissociation limit), part of the $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ band system. A constraint on the O_2 partial pressure of ~2×10^{-6} atm was derived by requiring that atmospheric sulfur be partitioned into both sulfate and elemental sulfur allotropes up to S_8 [5]. This constraint

arises from the relative rates of SO reaction with O_2 to reform SO_2, versus SO photolysis to release S atoms. For higher O_2 partial pressures, all sulfur species are oxidized to sulfate, as in the modern atmosphere.

Models of photolysis in optically thick columns of SO_2 in the atmosphere produce large mass-dependent fractionation (S-MDF) due to self-shielding by $^{32}SO_2$ [10], in contrast to the Archean rock record, which has comparable amounts of S-MIF and S-MDF. These large MDF signatures arise from the mass-dependent shifts in the absorption spectra of the isotopic SO_2 molecules [10]. Laboratory experiments verify these modeling predictions [8,11]. If SO_2 photolysis is the source of the Archean S-MIF, the column cannot be optically thick, which constrains the global mean SO_2 abundance to < 1 ppb. It has been suggested that differences in the magnitudes of the cross sections of sulfur isotopologues of SO_2 can account for the geochemical record of S-MIF [9], but evaluations of these cross sections in photochemical models argue against this interpretation [12]. An alternative hypothesis [13] combines SO_2 self-shielding [7] with fractionation in the non-dissociating $\tilde{B} \leftarrow \tilde{X}$ band system due to inter-system crossing [14]. This scenario requires a reducing atmosphere, with ~2% CO or CH_4. This is a fine-tuned scenario requiring a very high abundance of reducing gases, and as

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such we consider it an interesting but unlikely solution to the S-MIF problem. Modern ice core sulfates, produced during explosive volcanic eruptions and transported to the Antarctic and deposited in snow and ice layers, also exhibit small S-MIF signatures, but with proportionally larger S-MDF signatures [15,16]. The Antarctic ice core sulfates are in part consistent with a SO_2 self-shielding source in a stratospheric volcanic plume [8], but a non-volcanic source has also been suggested [17]. Pressure broadening may be important in laboratory experiments in which SO_2 is dissociated in the presence of a background gas (He) at pressures from 1 bar [8] up to 900 torr [18]. In these experiments, a decrease in S-MIF signature was noted for SO_2 at higher bath gas pressures, possibly a result of pressure broadening. Here, we measure pressure broadening in SO_2 at 215 nm, and compare to results previously determined for a different electronic excited state at 308 nm [19]. A simplified model is presented for the isotope fractionation effects of pressure broadening in dissociation of SO_2. Other reactions could account for the observed S-MIF in Archean rocks, including SO photolysis [10], SO radical reactions, and addition reactions of sulfur allotropes [20,21], but we focus in this work only on pressure broadening.

2. Experimental

The vacuum ultraviolet absorption spectrum of SO_2 is dominated by the strong and highly structured $\tilde{C}^1B_2 \leftarrow \tilde{X}^1A_1$ system spanning the 175–230 nm region. The spectrum is complex at room temperature, consisting of densely packed and often blended rotational lines within overlapping vibrational bands. Though the spectroscopic literature on this prominent system is extensive, a complete analysis of the absorption features has yet to emerge. References to earlier spectroscopic work can be found in the recent series of papers by Field and co-workers [22–25], and by Poirier and co-workers [26–28]. High-resolution photoabsorption cross sections have been reported at 295 K [29,30] and at 160 K [31].

Our pressure-broadening measurements focused on three groups of narrow lines in the strong vibrational band with a band head at ∼46,464 cm^{-1} and rotational structure spanning the 46,310–46,464 cm^{-1} region. These features near 215 nm were chosen for their strengths and unblended natures, and because broadening from predissociation is known to be minimal in comparison to lines at shorter wavelengths. The long-standing vibrational assignment for this band (and for other bands in the strong progression of bands characterizing the $\tilde{C} \leftarrow \tilde{X}$ spectrum) was recently shown to be in error in the two recent series of papers cited above. Kumar et al. [27] label the vibrational level of the upper state of this band $(v_1,v_2,v_3) = (2,0,4)$, though they qualify this assignment by indicating that there is significant mixing of other zero-order normal modes. For brevity, we will use the (2,0,4) label; the previous assignment of this band was (1,6,2).

The rate of SO_2 dissociation, measured by [32] and by [33], increases gradually above the threshold for predissociation at 45,725 cm^{-1} [34,35]. The natural line widths of the lines in this study (in the absence of pressure broadening) are determined by the sums of the radiative and dissociation rates. Katagiri et al. [32] report an experimental dissociation rate of ∼1×10^9 s^{-1} and estimate a radiative rate of 3.3×10^7 s^{-1}, resulting in a natural line width of ∼0.005 cm^{-1} (FWHM). Okazaki et al. [33] report a dissociation rate for the (2,0,4) band ((1,6,2) in their work) of 0.53×10^9 s^{-1}, leading to a natural line width of ∼0.003 cm^{-1}. The computed 295 K Doppler width of the measured lines is 0.072 cm^{-1}.

Preliminary line width measurements were carried out on the Imperial College London ultraviolet Fourier transform spectrometer [36], an instrument with a maximum resolution of 0.025 cm^{-1}.
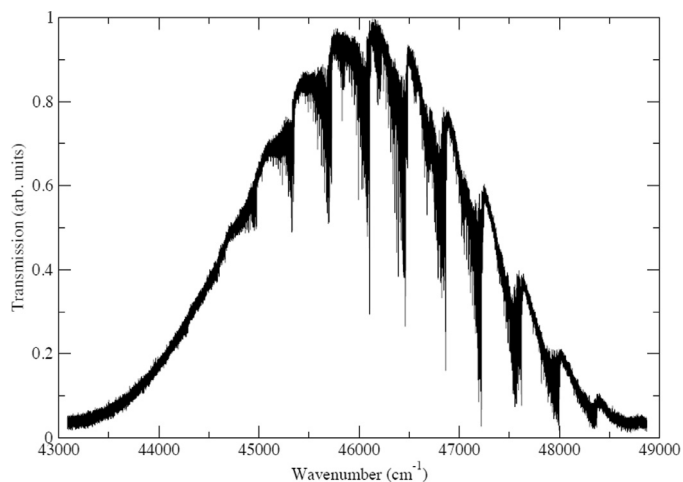

Fig. 1. Transmission spectrum over a full undulator bandpass for SO_2 at 0.094 mbar in a 40 cm absorption cell. FTS resolution on the DESIRS beamline at Soleil synchrotron is 0.11 cm^{-1}.

The definitive set of broadening measurements was recorded on the VUV-FTS on the DESIRS beamline of the Soleil synchrotron in St. Aubin, France [37,38] with a much higher signal-to-noise ratio. The VUV-FTS was operated at its maximum possible resolution of 0.11 cm^{-1}. The DESIRS undulator provided a continuum background with a 7% bandwidth (3200 cm^{-1} FWHM at 46,400 cm^{-1}). A xenon gas filter was used to remove high energy harmonics from the post-undulator synchrotron beam. Twenty five co-added scans typically resulted in a signal-to-noise ratio at the peak of the undulator bandpass of about 100.

The mixed-gas samples were prepared in a 5 l stainless-steel cylinder. The SO_2 and bath gas (either N_2 or CO_2) were pre-mixed in the cylinder, and then expanded into a 40 cm stainless steel absorption cell outfitted with MgF_2 windows. In addition to absorption scans of pure SO_2, used to establish the zero-broadened widths of the lines, two sets of broadening scans of SO_2 were taken: one set with an N_2 bath gas at 5 pressures (90.1, 233.3, 357.5, 503.0, and 738.7 mbar), and one set with a CO_2 bath gas at 4 pressures (101.6, 254.0, 350.9, and 501.3 mbar). The pure SO_2 scans were recorded at a pressure of 0.094 mbar; self-broadening is negligible at this pressure. Fig. 1 displays the full undulator bandpass of a pure SO_2 scan (25 co-adds) on the DESIRS beamline at Soleil. Fig. 2 indicates the positions of the three groups of measured lines in the (2,0,4) band, with line positions given in Table 1.

3. Results

Within the (2,0,4) rovibronic band, three clusters of lines were selected for analysis at 46,316 cm^{-1}, 46,338 cm^{-1}, and 46,406 cm^{-1}. Fig. 3 illustrates the broadening of the 46, 338 cm^{-1} cluster as the N_2 bath gas pressure is increased from zero to 739 mbar. For each feature within a cluster of lines, a least-squares fitting routine was used to determine a value for the Lorentzian component of the observed line profile, taking into account the effect of the finite instrumental resolution. All lines were modeled with Voigt profiles with Gaussian components of 0.072 cm^{-1} (FWHM) determined by room-temperature Doppler broadening. The instrument function is described by a sinc function (0.11 cm^{-1} FWHM), which results from the finite path difference in the recorded interferogram [39]. By varying the position, line strength, and Lorentzian width of each feature, the least-squares fitting routine minimizes the difference between a model transmission spectrum (calculated by a convolution of the line's Voigt profile in absorption with the instrumental sinc function) and the measured transmission spec-