High-Resolution B-band (240-320 nm) Spectroscopic Measurements of Sulfur Dioxide Isotopologues and Its Isotopic Effect Study

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Abstract

Sulfur dioxide (SO_2) injected into stratosphere during huge volcanic eruptions produces stratospheric sulfate aerosol (SSA), which exhibits sulfur mass-independent fractionation (S-MIF) from collected Antarctic and Greenland ice cores. S-MIF is expected as a tracer of past eruptions, which could significantly impact climate. However, S-MIF origin in SSA remains controversial and once it is constrained, S-MIF will become a unique proxy of past stratospheric chemistry at huge eruptions. Previous measurement at low resolution (8 cm^{-1}) predicted $\Delta^{36}S/\Delta^{33}S$ slope of ~-4, well matching the SSA characteristics. However, SO_2 photoexcitation experiments (namely, isotope ratio measurements of the products in UV irradiation to natural abundance SO_2) show $\Delta^{36}S/\Delta^{33}S$ of ~+1, contrasting results from spectrum measurements. Electron transitions and sophisticated vibrational and rotational energy levels causes rovibrational structures in SO_2 UV spectrum, the lack of resolution may have affected the accuracy of S-MIF calculations. This study optimized an experiment setup and used the least absolute deviation (LAD) linear regression for data calibration to measure the $^{32,33,34,36}SO_2$ B^1B_1-X^1A_1 absorption spectrum (240-320 nm) with a resolution of 0.4 cm^{-1} and 3-10% error. LAD method significantly reduces the error in low signal-to-noise region than the conventional averaging method during cross-sections calculations. Small S-MIF in SO_2 photoexcitation alone is predicted, supporting a hypothesis that the S-MIF produced during SO_2 photoexcitation experiments is produced by the intersystem crossing processes rather than photoexcitation alone. Self-shielding calculations from this study show the altitude variability does not produce any significant $^{36}E/^{33}E$ slope but shows an overlap with volcanic data, suggesting that the ^{36}E variability is produced by altitude. Also, the results are consistent with the altitude and self-shielding calculations with opposite signs.

Early Career Scientist

YES, I am an early career scientist.

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