

SO₂ 紫外線スペクトルにおける圧力及び同位体効果

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Pressure and Isotopic effects on the ultraviolet Spectra of SO₂
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Introduction.

Most chemical reactions produce mass dependent isotopic fractionation while Sulfur Non-Mass Dependent (NMD) fractionation signals reported (Fig.1) for the Archean and Early Proterozoic (>2300 Ma). The photodissociation of sulfur bearing species may have played a significant role since the concentration of oxygen is estimated to be 10⁻⁵ times present atmospheric levels and therefore ultraviolet light permeates throughout the entire atmosphere, however the underlying mechanisms are not fully understood. Understanding the mechanism of sulfur isotopic fractionation during the photodissociation of SO₂ in reducing atmospheres is important for interpreting the geological record describing the rise of oxygen. In this report we present newly obtained data sets from experimental measurements and theoretical calculations. From the comparison of theoretical and experimental dates we discuss the limit the spectral resolution needed to obtain a fully resolved spectrum and also how atmospheric pressures affect isotopic effects during the photodissociation reaction.

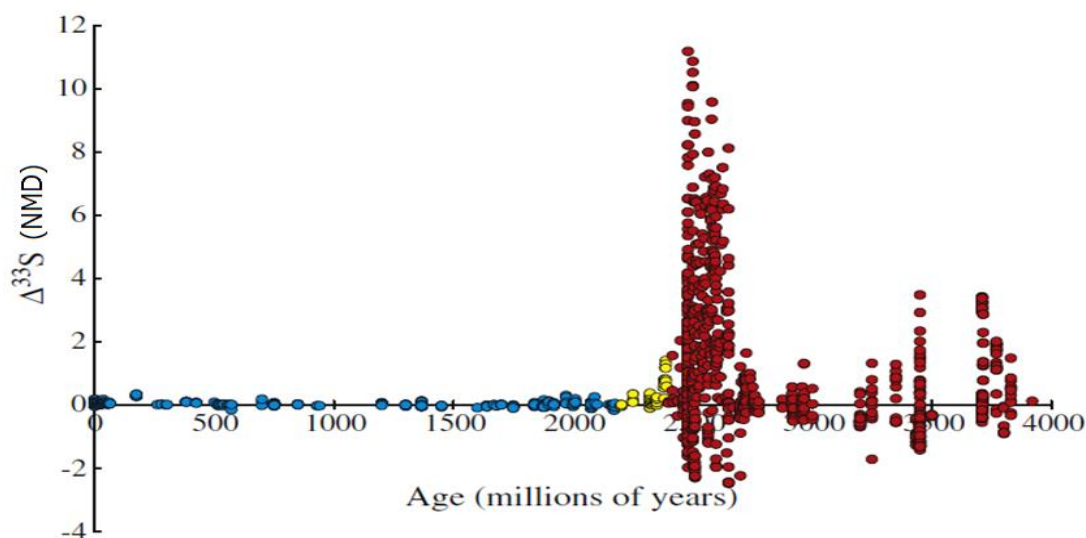


Fig. 1 NMD signal preserved in the geological record (Fig. adopted from Masterson *et al.*¹)

Experimental.

We used a dual beam monochromator in order to obtain higher accuracy cross section that is complementary to high spectral resolution Fourier transform spectrometer and previously reported [1]. High-precision and high-accuracy data of the ultraviolet absorption cross sections of $^{32}\text{SO}_2$, $^{33}\text{SO}_2$, $^{34}\text{SO}_2$ and $^{36}\text{SO}_2$, recorded 190 to 225nm at room temperature, with slit width of 0.1nm, data interval of 0.02nm. SO_2 samples were produced in an identical process via combustion of isotopically enriched S^0 , eliminating effects due to variation in oxygen isotopic composition. Our measurements show red shifted peak position for heavier isotopologue relative to the $^{32}\text{SO}_2$, though rotational structures cannot be observed due to low spectral resolution we use these spectra to combine the analysis with theoretical calculations.

Theoretical.

In the present work, we performed a theoretical analysis of photolytic isotopic fractionation factors with a first principle simulation. The ultraviolet absorption cross sections were computed using the wave packet propagation technique to explore the influence of excited state dynamics, transition dipole surface and initial vibrational state. The wave-packet propagation technique used here was the “real wave packet” method². Jacobi coordinates were employed to describe the relative position of the three nuclei in the body fixed plane. The wave packet is represented using evenly spaced Fourier grids for R and r coordinates, and associated Legendre polynomials based discrete variable representation (DVR) for the angle θ . We calculated the vibrational wave functions of the ground state using the Lanczos method. After constructing the initial wave packet, the time evolution on several PES were calculated and the autocorrelation function was computed by numerically integrating the product of the initial wave packet and the wave-packet at each time step. Total photo-dissociation cross section as a function of the excitation energy was computed as the Fourier transform of the autocorrelation function as a function of time. We compare calculated spectra for each isotopologue with experimental data and present an attempt to construct a rotationally resolved spectra.

References.

- [1] J. F. Kasting, *SCIENCE*, **293**, 819-820 (2001)
- [2] Gray and Balint-Kurti, *J Chem. Phys.*, *108*, 950 (1998).