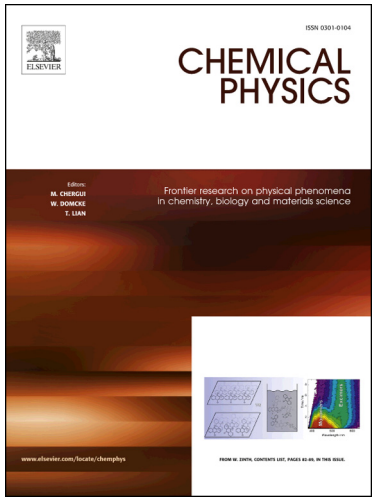

"Theoretical study of electronic properties and isotope effects in the UV absorption spectrum of disulfur"

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"Theoretical study of electronic properties and isotope effects in the UV absorption spectrum of disulfur[⋆]"

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Abstract

The electronic structures of triplet S_2 ground and excited states are studied by *ab initio* molecular orbital and configuration interaction calculation. Potential energy curves correlated with $S(^3P) + S(^3P)$ and $S(^3P) + S(^1D)$ at the dissociation limit are evaluated, and electronic terms for a total of 11 states are assigned. Transition dipole moments, as a function of internuclear distance, are determined for two allowed transitions to $B''^3\Pi_u$ and $B^3\Sigma_u^-$ excited states. The total absorption cross-sections are computed to estimate isotope-fractionation constants, ε, for four most common isotopologues: $^{32}S^{32}S$, $^{32}S^{33}S$, $^{32}S^{34}S$, and $^{32}S^{36}S$ by quantum close-coupling (R-matrix) expansion approach and they are found to lie in a mostly opaque to competing absorbers spectral window. We suggest that the photochemistry and isotopic effects of S_2 are of significant importance and provide data showing high sensitivity of mass-independent fractionation to excitation wavelength. Zero-point energy based constants ε^{ZPE} are estimated as well to compare with the obtained isotope effects and two modes for MIF are present in three-isotope plots; large isotopic effects were observed for both ^{36}S and ^{33}S with an excitation wavelength-dependent fluctuation.

Keywords: potential energy curves, absorption cross-section, photodissociation, isotope effects

1. Introduction

Most sulfur trace molecules have a strong absorption in 180–300 nm range.[1, 2, 3, 4] As a result, in the present atmosphere most tropospheric sulfur-containing molecules are shielded from UV radiation by the ozone layer and undergo oxidation to sulfuric acid and formation of sulfate particles. The photochemistry introducing mass-independent isotopic fractionation (MIF) effects is limited to high altitudes and the isotopic constitution of washed out sulfates has a close resemblance to the emitting source. However, before the oxygen levels rose and stabilized in the atmosphere, approximately 2.5 Ga ago, a large fluctuation in sulfur isotope abundance was observed. During the Archean period the lack of oxygen in atmosphere created a significant increase in actinic flux of shorter wavelengths,[5] leading to a large increase in photochemical activity of atmospheric sulfur. The major sources of sulfur-containing molecules were volcanic eruptions and outgassing, and marine outgassing; mostly in a form of SO_2 and H_2S.[6, 7, 8, 9] Due to the increased solar flux in mid-UV range in anoxic atmosphere, sulfur compounds undergo several reducing photodissociation steps: sulfur dioxide is photolyzed to SO + O which undergoes photolysis again to produce S + O; skewing the ratio of isotopologues due to MIF.[2, 4, 10, 11] Sulfur

[⋆]Electronic Supplementary Information (ESI) available online.
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