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非断熱遷移計算による SO の紫外線スペクトル II：同位体と圧力効果

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Nonadiabatic calculations of ultraviolet absorption cross-section of sulfur Monoxide II: Isotopic and broadening effects

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Introduction.

Sulfur monoxide (SO) has been studied for many years. This system is suitable for theoretical calculations which have been used to explore many of its molecular properties, among them light absorption parameters. The chemical reactivity of SO makes it difficult to conduct experimental studies. The implications of SO photochemistry extends over a wide range of areas such as interstellar chemistry, molecular clouds, and the atmospheric photochemistry of Jupiter's satellites. In the terrestrial Archean atmosphere the photo-dissociation of SO_2 plays an important role in the atmospheric sulfur cycle[1]. The main product of SO_2 photodissociation, SO, is consequently an important factor in understanding the Archean sulfur cycle and the isotopic imprint in the geological record[2]. In these geochemical scenario the study of SO photochemistry induced by ultraviolet spectra and the isotopic fractionations during photo-dissociation are key to unravel the atmospheric composition of the primitive Earth. Numerous theoretical and experimental studies of numerous SO electronic states such as $a^1\Delta$, $b^1\Sigma^+$, $A^3\Pi$, $B^3\Sigma^-$ and their electronic transitions from the ground state $X^3\Sigma^-$ have been reported in the literature. Despite the abundance of calculations at high theoretical level there is no report in the literature of theoretically calculate ultraviolet absorption cross-sections relevant to the study of photochemistry in planetary atmospheres. We set out to calculate ultraviolet absorption cross sections of sulfur isotopologues ^{32,33,34,36}SO by *ab-initio* methodology and conclude on the isotopic effects produced by the ultraviolet absorption spectra.

Methods.

The employed procedure is common to many theoretical studies of ultraviolet spectra produced by electronic excitations. The MOs were determined by complete active space self-consistent field (CASSCF) calculations, once the MOs were obtained, multi-reference configuration interaction (MRCI) calculations were performed by using the diffusion-function-augmented, correlation-consistent, polarized-valence sextuple-zeta (AV6Z also known as aug-cc-pV6Z) basis functions resulting in a total of 382 contracted functions. Once electronic energies, transition dipole moments and non-adiabatic couplings were calculated a R-matrix expansion was used to calculated absorption cross-sections of the main absorption transitions.

In this work we concentrated on specific robrational states to recreate a more realistic spectrum suitable for atmospheric modeling.

Results.

The calculated absorption cross-section of $^{32}S^{16}O$ reproduces well the only one experimental spectrum available in the literature. The spectral feature and the absolute values of photoabsorption cross sections are also in good agreement. Our calculations predicts three different bands (Fig. 1c), a progression starting at the band origin, a resonant state and a continuous band. This long lived photoexcited SO* specie that has not been directly reported previously in the literature nor its implications for the atmospheric have been discussed. This finding is of great importance for atmospheric modeling since it spawns an entire set of the chemical reactions that may affect the balance of stable species. The isotopic effects are also of relevance since each of the segments presented above cause different types of isotopic effects that ranges from large non-mass dependent in the resonant states to largely mass-dependent in the continuous band.

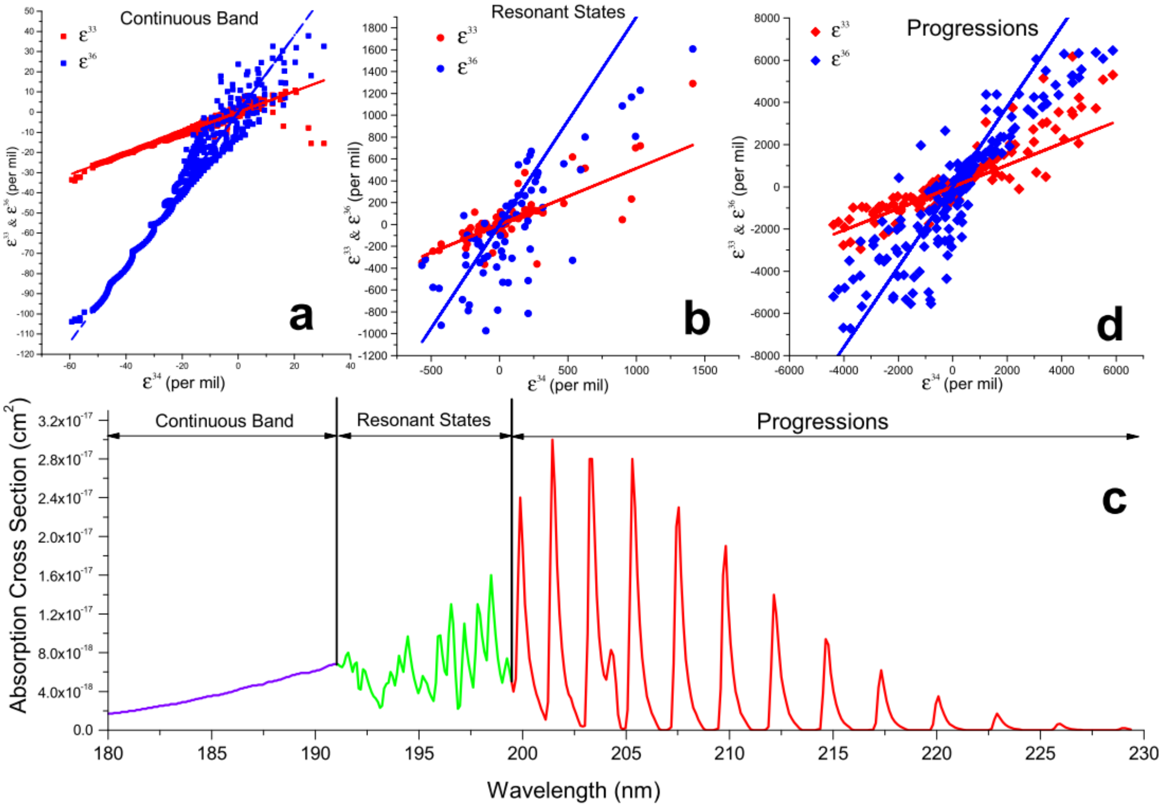

Fig. 1. Calculated SO spectra (panel C), continuous band, resonant states and vibrational progressions. Panels A to B show the isotopic distributions at each spectral segment.

References.

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[2] J. Farquhar, H. Bao and M. Thiemens, *SCIENCE*, 289, 756 (200).