Theoretical Investigation of Electronic Properties of Gaseous Disulfur

(*Sophia University) ◯<u>Karolis Sarka</u>*,‡, Sebastian O. Danielache*, Shinkoh Nanbu*

Introduction

In Archean atmosphere, a large discrepancy in the abundance of stable sulfur isotopes has been observed. The isotope anomaly has significantly changed upon increase in oxygen levels in the atmosphere, and during the Great Oxygenation event, it reached stable values and remained constant until present times. According to Kasting,[1] under anoxic conditions the prevalent sulfur chemistry in the atmosphere is the cyclic photochemical reaction: S $\longleftrightarrow$ S_2 $\longleftrightarrow$ S_4 $\longleftrightarrow$ S_8, where forward-reaction is propagated by combination with the same compound and the backward path is initiated by photodissociation. The nonadiabatic crossings in the photodissociation mechanisms of the molecules would be the source of mass-independent isotopic fractionation (MIF). In this study we present the computational results for potential energy curves (PECs), found non-adiabatic crossing, and assigned electronic states for S_2.
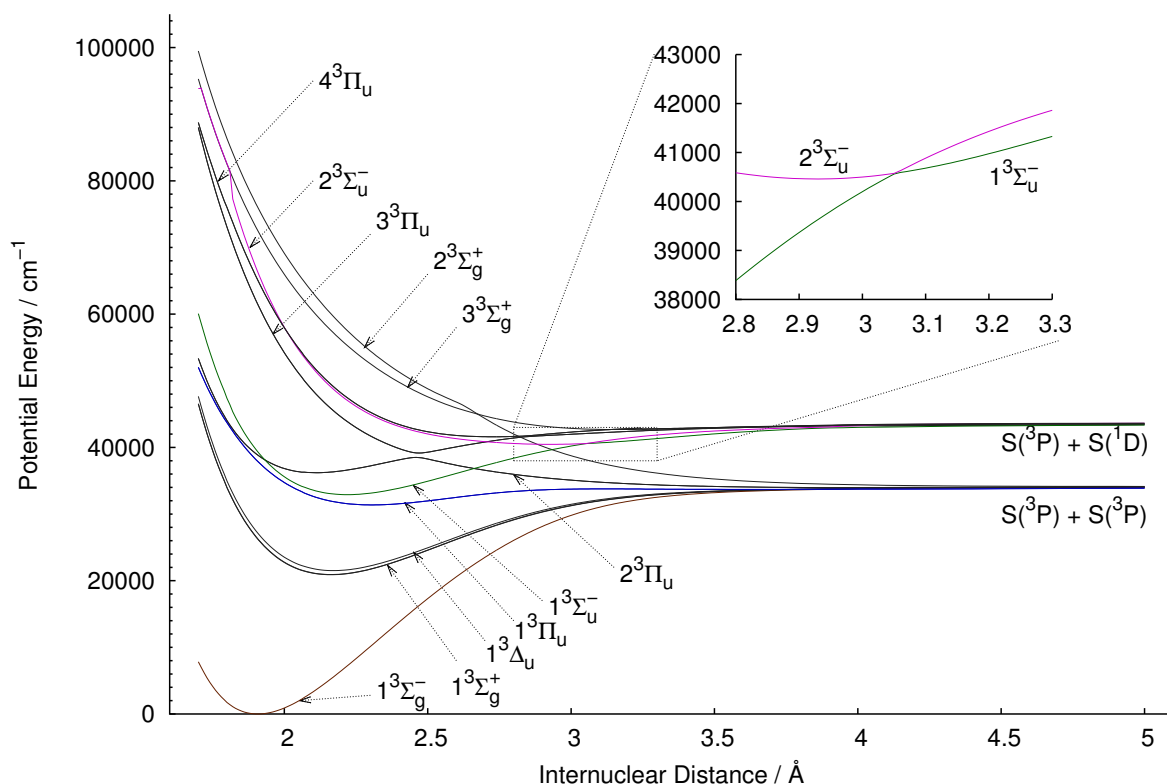
Results and Discussion

Figure 1: Potential energy curves of the electronic ground and excited states for S_2. Brown curve – ground state; colored curves denote PECs with allowed transition from ground state. Blue curve: $1^3\Pi_u$ state; green curve: $1^3\Sigma_u^-$ state; magenta curve: $2^3\Sigma_u^-$ state. Magnified – conical intersection.

The global PECs were determined at MRCI-F12 level calculations with aug-cc-pVQZ basis set, using MOLPRO2012 software package. A fine spatial grid was chosen (0.01 Å) to accurately evaluate the exact

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‡E-mail to: ksarka@eagle.sophia.ac.jp
[1]Kasting, *Science*, **293**, 5531, 2001.

Table 1: S$_2$ electronic state comparison in term energy without zero-point vibrational energy on theory

Electronic Term	Energy, cm^{-1}		Equilibrium Radius, Å	
	Theory	Experiment	Theory	Experiment
$1^3\Sigma_g^-$	0	0	1.91	1.889[2]
$1^3\Pi_u$	31371.71	31070[2]	2.31	2.3[2]
$1^3\Sigma_u^-$	32909.66	31830[2]	2.22	2.17[2]
$2^3\Sigma_u^-$	40459.54	55582[2]	2.93	
		55658.29[3]		
		55598.2[4]		

avoided curve-crossing (ACC) point between various states. For our study, we only look at symmetry-allowed transitions and the single ACC point between the $1^3\Sigma_u^-$ and $2^3\Sigma_u^-$ states. The PECs are shown in Fig. 1

The ACC at 3.055 Å was found to be the source for sulfur isotope MIF in atmosphere under anoxic conditions. The nonadiabatic coupling matrix elements (NACMEs) were computed using the DDR procedure in MOLPRO2012, forming the matrix from wavefunctions and transition density matrices at reference geometry and slightly displaced ($r \pm dr$) geometries. The NACMEs were observed to feature a discontinuous function, localized around the conical intersection $\lim_{r \to r_{\text{CoIn}}} f(r) = \pm\infty$.

As can be seen in Table 1, our results agree quite well with the experimental data for the $1^3\Pi_u$ and $1^3\Sigma_u^-$ states. In higher energy range, all previous experimental data[2–4] predict that the energy of $2^3\Sigma_u^-$ state is approximately 15'000 cm^{-1} higher than our result; we strongly suspect that it would be due to misassignment of electronic states performed in the experiments. Since the published data regarding the electronic excitations is severely limited, no further comparison is available at the moment.

Conclusions

We have computed the potential energy surfaces for S$_2$ with three excited states that have symmetry-allowed transitions from the ground state. An avoided curve-crossing point was found between $1^3\Sigma_u^-$ and $2^3\Sigma_u^-$ states at 3.055 Å. The energy levels and equilibrium interatomic distances agree well with experimental data.

Further goals include the computation of an absorption cross section spectrum and quantifying the magnitude of mass-independent fractionation caused by this reaction.

[2]Radzig *et. al.*, Reference Data of Atoms, Molecules, and Ions. *Springer-Verlag*, 1985
[3]Barrow *et. al.*, *J. Phys. B: At. Mol. Phys.*, **2**, 413, 1969
[4]Maeder *et. al.*, *Nature*, 4089, 1948