

Calculation of absorption cross-sections and isotopic effects in photochemistry of S₂ and S₃

oKarolis Sarka^{1,‡}, Shinkoh Nanbu¹

¹Department of Materials and Life Sciences, Sophia University, Japan

Introduction

The photochemistry of elemental sulfur is one of the few unsolved questions in the photochemistry of atmospheres of late Archean period[1], Venus[2], Io[3], and other extraterrestrial atmospheres. It is prohibitively difficult to measure the spectra of fine-structure in ultraviolet due to the high temperature requirement for vaporization of elemental sulfur. For complete picture of the elemental sulfur photochemistry the photochemical cycle can be written down as: $S \longleftrightarrow S_2 \longleftrightarrow S_4 \longleftrightarrow S_8$; however, there are additional quasi-stable intermediate complexes present, thus we have to consider S₃, S₅, S₆, and S₇ compounds as well. Due to the number of degrees of freedom, at the present it is only possible to obtain exact solutions for S₂ and we are developing a solution for S₃. The sulfur dimer and trimer systems are isoelectronic to the oxygen and ozone cycle, and it is very likely that the sulfur undergoes a *Chapman mechanism*-like cycling in an anoxic atmosphere as well, reinforcing the isotopic fractionation occurring at each step.

To avoid the obstacles in experimental measurement, we turn to exact calculations of spectra based on time-independent Schrödinger equation, using R-matrix propagation of time-independent wavefunctions across the global potential energy curves for all discrete vibrational and rotational states and a combination of R-matrix and S-matrix for the continuum region.

Results and Discussion

We present the fine-structure spectra for sulfur dimer and its isotopologues as a sample of 1D system, including the precise source of mass-independent isotopic fractionation for compounds with low density-of-states. The potential energy curves and transition dipole moments are calculated at MRCI-F12/aug-cc-pVQZ level at full valence active space; absorption spectra are calculated for two lowest states with an allowed transition from the ground state ($X^3\Sigma_g^-$) – $B''^3\Pi_u$ and $B^3\Sigma_u^-$.

Based on the shifted fine-structure for each isotopologue, we have observed a strong excitation wavelength dependency for the mass-independent isotopic fractionation. It is clear that accurate evaluation of isotopic fingerprint for the atmospheric photochemistry of elemental sulfur needs a precise modeling setup, with spectral resolution approaching that of a natural broadening of a single absorption peak. The effects are also very susceptible to the shielding of competing absorbers and self-shielding. It is important to note that within a specific, narrow wavelength range, the molecule can exhibit both enriching and depleting isotopic effects, and this bimodal distribution of isotopic fractionation factor can be seen in three-isotope plot, Fig. 1. Strong dependency on specific wavelength of transition indicates that it is not acceptable to just assume a single value for a specific isotopologue – the evaluation must be performed carefully with a significant attention to detail.

[‡]E-mail to: ksarka@eagle.sophia.ac.jp

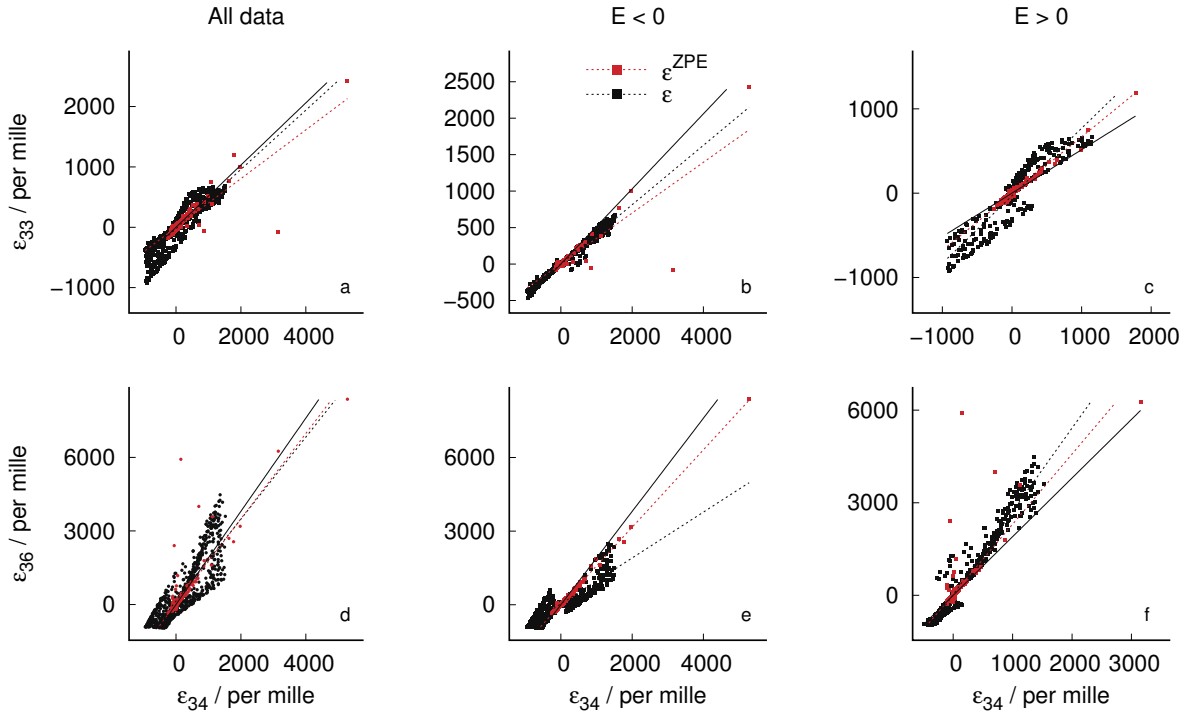


Figure 1: Three-isotope plots of $\epsilon_{33}(\epsilon_{34})$ (a-c) and $\epsilon_{36}(\epsilon_{34})$ (d-f). Solid lines represent MDF lines, dashed lines represent NLLS fit of the data. The data is split based on MIF factor E .

To evaluate the absorption cross-section of triatomic molecules we are developing a time-independent method based on proven theories of reactive scattering and ro-vibrational spectra calculation. The proposed mechanism is to solve the hyperspherical Schrödinger equation for each potential surface using a diabatic-by-sector approach, and to propagate the wavefunctions obtained at each sector over complete surface using the R-matrix theory. Once the wavefunctions and eigenenergies are known, the remaining calculation of the absorption cross-section is trivial.

Conclusions

The spectra and mass-independent isotopic fractionation analysis indicate that sulfur dimer could play an important role in Archean earth and various extraterrestrial bodies. There is an ongoing search for unidentified absorbers and the spectral peak of S_2 lies precisely in the window that has few competing absorbers in an anoxic atmosphere. The feedback loop through S_3 is worth exploring and it might produce a significant isotopic fingerprint for elemental sulfur.

References

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