One Possible Source of Mass-Independent Fractionation of Sulfur Isotopes in the Archean Atmosphere of Earth

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Abstract: Energy transfer mechanism for recombination of two sulfur atoms into a diatomic molecule, S_2 , is studied theoretically and computationally to determine whether the rate coefficient of this process can be significantly affected by isotopic substitutions, and whether the resultant isotope effect is expected to be mass-dependent or mass-independent. This is one of sulfur polymerization processes thought to be important in the anoxic atmosphere of the Archean Earth and, potentially, relevant to mass-independent fractionation of sulfur isotopes. A simplified theoretical approach is employed, in which all properties of S_2 molecule are characterized rather accurately, whereas the process of stabilization of metastable S_2^* by bath gas collisions is described approximately. Properties of individual scattering resonances in S_2 are studied in detail, and it is found that most important contributions to the recombination process come from ro-vibrational states formed near the top of centrifugal barrier, and that the number of such states is about 50 (in $^{32}S^{32}S$). Absolute value of recombination rate coefficient is computed to be $1.22 \times 10^{-33} \text{ cm}^6/\text{s}$ (for $^{32}S^{32}S$ at room temperature and atmospheric pressure), close to experimental result. Two distinct isotope effects are identified. One is a classical mass-dependent effect due to translational partition function, which leads to a weak, smooth, and negative mass-dependence of rate coefficient (4% decrease when the mass is raised from $^{32}S^{32}S$ to $^{34}S^{34}S$). Second effect, due to quantized resonances, is two orders of magnitude stronger, but is local. In practice, due to presence of multiple individual resonances, this phenomenon leads to irregular mass-independent variations of rate coefficients in the ranges $\pm 5\%$. It is also demonstrated that in real molecules this irregular behavior is expected to be somewhat smoother, and the isotope effect is somewhat smaller, due to dependence of stabilization cross section on properties of individual resonances (not described by present model). Thus, additional calculations of stabilization cross sections are needed in order to give quantitative prediction of this mass-independent isotope effect, and to determine its relevance to mass-independent fractionation of sulfur isotopes in the Archean rock record.

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I. Introduction

Diverse chemistry of gas phase sulfur played important role in the anoxic atmosphere of Archean Earth (Kasting et al., 1989; and Kasting, 2001), when volcanic eruptions served as sources of H₂S and SO₂ (oxidation states of sulfur are -2 and +4, respectively). It is believed that at low concentrations of atmospheric oxygen, specific to Archean atmosphere, photolysis of these gases produced atomic S that entered a sequence of recombination reactions, responsible for substantial production and deposition of elemental sulfur (oxidation state is zero), S₈ (Young, 1985; Kasting et al., 1989):

Here M represents a chemically neutral bath gas (e.g., N₂ in the atmosphere). In contrast to this behavior, in the oxygen-rich atmosphere, as we have today, most of the sulfur would be oxidized, removed from the atmosphere by rain-out and incorporated into the oceanic water as sulfate (oxidation state is +6). This difference in chemistry gives geoscientists a practical tool for understanding the evolution of Earth's atmosphere based on interpretation of geological rock record (Rumble, 2005). In particular, analysis of isotopic enrichments of sulfur and oxygen in the Archean deposits led to discovery of a striking mass-independent fractionation effect (Farquhar et al., 2000a; Farquhar and Wing, 2003; and Farquhar et al., 2003), that provided key element for pinpointing the time of great oxygenation event and for deriving atmospheric conditions at the time when the early life emerged (Kasting et al., 1989; Kasting, 2001; Rumble, 2005).

However, molecular level origin of this mass-independent fractionation effect for four stable isotopes of sulfur (S-MIF) is not yet clear, and it is quite possible that several mechanisms of isotopic enrichment took place in the Archean atmosphere simultaneously, producing different features of S-MIF observed in the rock record today. One of the widely tested hypothesis involves UV photolysis of SO₂ (Farquhar et al., 2000b, Farquhar et al., 2001, Lyons, 2007, Lin et

al., 2011, and Ono et al., 2013, Whitehill et al., 2015), which may also include non-adiabatic molecular dynamics processes that followed photoexcitation (Whitehill et al., 2013). Another hypothesis worth testing relates to the recombination reactions (1-5) that may be quite sensitive to isotopic substitutions, by analogy with recombination reaction that forms ozone: $O_2 + O \xrightarrow{+M} O_3$, that is known to produce large O-MIF effect in today's atmosphere, which is well documented (Thiemens, 2006, Thiemens, 2007, and Thiemens et al., 2012) and is much better understood mechanistically, from both experimental (Janssen et al., 2001, and Mauersberger et al., 2003) and theoretical (Gao and Marcus, 2001, Babikov et al., 2003a, Babikov et al., 2003b, Schinke and Fleurat-Lessard, 2005, Grebenshchikov and Schinke, 2009, and Ivanov and Babikov, 2013) perspectives. Such *recombinative* origin of S-MIF is explored in this paper, for the first time.

Kinetic models of sulfur cycle in the early atmosphere of Earth (Kasting, 1990, Pavlov and Kasting, 2002, and Calirre et al., 2014) incorporate about 100 chemical and photochemical reactions of the sulfur bearing species, including recombination processes (1-5), and the chemical reaction that produces the smallest sulfur allotrope, $S + SH \rightarrow S_2 + H$. Such chemical models could serve as a quantitative tool for testing various mechanisms of S-MIF generation, deposition and preservation, provided a reliable set of input data is available – the rates of individual reactions. Unfortunately, it should be admitted that the rates of sulfur recombination reactions (1-5) are largely unknown. Experimental data are sparse and often controversial (Fawlers et. al., 1967, and Nicholas et al., 1979) while theoretical predictions are incomplete (Francisco et al., 2005, Peterson et al., 2006, Du et al., 2008, Du et al., 2011). Isotope effects in these recombination reactions have never been studied.

Namely, a closer look at the recombination rate coefficients used in the literature (Kasting, 1990, Pavlov and Kasting, 2002) reveals that the rate coefficient of reaction (1) for recombination of two sulfur atoms: $\kappa_1 = 2.99 \times 10^{-33} \text{ cm}^6/\text{s}$ (at 298 K), is simply taken equal to the rate of similar reaction with oxygen atoms: $O + O \rightarrow O_2$. The rate coefficient of reaction (2): $\kappa_2 = 2.8 \times 10^{-32} \text{ cm}^6/\text{s}$, is estimated based on a similar ozone forming reaction: $O_2 + O \rightarrow O_3$, by reducing its rate coefficient by an empirical factor. The rates of reactions (3) and (5) are made equal to the rate of reaction (4), that was also determined indirectly, so: $\kappa_3 = \kappa_4 = \kappa_5 = 2.8 \times 10^{-31} \text{ cm}^6/\text{s}$. Finally, the isotope effects are introduced statistically, using the rotational symmetry

numbers for symmetric vs. asymmetric species, which can only be viewed as zeroth-order treatment. Clearly, this situation has to be updated.

Several steps have already been made towards theoretical description of the simplest recombination reactions of sulfur. Classical trajectory study of collision-induced dissociation of S_2 in the bath of Ar was carried out: $S_2 + Ar \rightarrow S + S + Ar$, and then used to derive the rate of reaction (1) by employing the principle of microscopic reversibility (Du et al., 2008). The value of $\kappa_{3B} = 4.19 \times 10^{-33} \text{ cm}^6/\text{s}$ was reported, that agrees reasonably well with experimental result of Nicholas et al., 1979: $\kappa_{\text{exp}} = 2.8 \times 10^{-33} \text{ cm}^6/\text{s}$, but disagrees by four orders of magnitude with that of Fawlers et. al., 1967 (measured in the bath of H_2S at 295 K). Although this theoretical prediction is close to some experimental data, and to the rate coefficient used in the kinetics models, one should keep in mind that such classical trajectory calculations can give only a contribution of non-resonant, *direct three-body* recombination process:

which dominates over other known mechanisms of recombination only if the pressure of bath gas (here Ar) is very high. In the low-pressure regime, typical to the atmosphere of Earth, the contributions of *energy-transfer* (Lindeman) mechanism:

and of the *radical-complex* (or “chaperon”) mechanism:

are expected to be more important. Here S_2^* is quantum scattering resonance while MS^* is a weakly bound van der Waals complex, both are metastable intermediate species, formed at the first step of the process. Stable S_2 is produced at the second step, when energy is carried away by the bath gas atom M. These major recombination mechanisms have never been studied for S_2 .

For S_3 , some features of the potential energy surface (PES) were mapped out (Francisco et al., 2005, Peterson et al., 2006), but the global PES, suitable for computational studies of

reaction dynamics in the recombination process $S_2 + S \rightarrow S_3$, was not built so far. The chaperon mechanism of recombination, in the Ar bath:

was studied using classical trajectory simulations (Du et al., 2011), and gave the rate of $\kappa_{ch} = 2.66 \times 10^{-33} \text{ cm}^6/\text{s}$. No calculations for the energy transfer mechanism, $S_2 + S \rightleftharpoons S_3^* \xrightarrow{+M} S_3$, were carried out.

Note that neither of previous theoretical studies of sulfur recombination involved isotopes other than ^{32}S . And neither of them can serve as a complete prediction of the recombination rate for S_2 or S_3 , since only one mechanism was considered in each case. No calculations for larger allotropes of sulfur were reported, to our best knowledge.

Ideally, contributions of all recombination mechanisms (energy-transfer, direct three-body and chaperon) should be predicted in a consistent manner and added together. But this is a very challenging problem, since the lifetimes and energies of scattering resonances (such as in S_2^* and S_3^*) and inelastic cross sections for their quenching by bath-gas particles (such as Ar) have to be determined from quantum calculations, and those are very demanding for heavier particles. It should be noted that there are no ready-to-use computer codes that would handle various mechanisms of recombination simultaneously, and even the choice of suitable theory framework is not obvious.

In this paper we make one step towards this goal, and carry out first calculations of the energy-transfer mechanism for production of S_2 , reaction (7), in the bath gas of Ar and for all four stable isotopes of sulfur: ^{32}S , ^{33}S , ^{34}S and ^{36}S . The focus is on the first step in the process (7) -- formation and decay of scattering resonances S_2^* , which is described rather accurately here and is explored in great detail. The second step in (7) -- stabilization of scattering resonances by bath-gas collisions, is treated approximately. Thus, our results are still preliminary, and the rates we report can't really be plugged into the kinetics modeling yet, but they demonstrate where the mass-independent isotope fractionations could come from. Some of our findings are quite unexpected and are important for explanation of the molecular level origin of S-MIF.

Why do we emphasize scattering resonances S_2^* ? Note that both the chaperon mechanism (8-9) and the three-body mechanism of recombination (6), as well as the second step of the energy-transfer mechanism (7), all involve a continuous motion of heavy particles. These are classical processes that depend on masses of the particles smoothly, and are not expected to exhibit mass-independent isotope effect (Ivanov and Schinke, 2006). In contrast, energies of scattering resonances (formed only at the first step of the energy-transfer mechanism of recombination) are quantized, and their lifetimes are very sensitive to the masses of particles. It is well known that a single resonance near threshold of the process can increase the rate of recombination by orders of magnitude (see, for example Inouye et al., 1998, Esry et al., 2003, and references there in). Furthermore, it is known that in ozone formation, that is also a recombination process, resonances play major role and are responsible for the O-MIF (Babikov et al., 2003a, Babikov et al., 2003b, Grebenshchikov and Schinke, 2009, and Ivanov and Babikov, 2013, Sun et al., 2015, Ivanov and Babikov, 2016). So, it seems to be important to explore by how much the individual resonances can affect recombination processes of sulfur (1-5), starting with the simplest reaction and going progressively down the list.

II. Theoretical Framework

II-A. Reaction Mechanism

Kinetics of the process (7) is described within micro-canonical framework, where different scattering resonances of S_2^* are treated as different chemical species (Babikov et al., 2003b, Pack and Walker, 2004, Grebenshchikov and Schinke, 2009, Ivanov and Babikov, 2013, Ivanov and Babikov, 2016). For each scattering resonance $S_2^{(i)}$ at energy E_i the processes affecting its population $[S_2^{(i)}]$ are considered and the corresponding rate constants are introduced. Those are:

- i) Formation of $S_2^{(i)}$ from atomic sulfur characterized by the second-order rate coefficient

$$k_i^{\text{form}}:$$

ii) Spontaneous unimolecular decay of $S_2^{(i)}$ onto S+S characterized by the first-order rate coefficient k_i^{dec} :

iii) Stabilization of $S_2^{(i)}$ by collision with bath gas atom, here Ar, characterized by the second-order rate coefficient k_i^{stab} :

iv) Collision-induced dissociation $S_2^{(i)}$ onto S+S characterized by the second-order rate coefficient k_i^{diss} :

Decay rate coefficients of quantum scattering resonances $S_2^{(i)}$ are directly given by their widths, $k_i^{\text{dec}} = \Gamma_i$, computed as explained in Sec. II-C. The coefficient of formation k_i^{fom} for each scattering resonance is related to its k_i^{dec} through micro-canonical equilibrium constant: $k_i^{\text{fom}} = k_i^{\text{dec}} K_{\text{eq}}(E_i)$. Such equilibrium constants $K_{\text{eq}}(E_i)$ for each scattering resonance $S_2^{(i)}$ are computed statistically, using known formula as covered in Appendix. The values of rate coefficients k_i^{stab} and k_i^{diss} are computed from the corresponding cross sections:

$$k = \left(\frac{8kT}{\pi \mu} \right)^{1/2} \times \sigma(T). \quad (16)$$

Here μ is $S_2 + \text{Ar}$ reduced mass. Based on results of unpublished simulations of $S_2 + \text{Ar}$ collision dynamics (using the mixed quantum/classical theory, Babikov and Semenov, 2016) the values of $\sigma^{\text{stab}} = 83.0 \text{ \AA}^2$ and $\sigma^{\text{diss}} = 37.6 \text{ \AA}^2$ were adopted for all scattering resonances in this work, irrespectively of their energy, ro-vibrational content or isotopic composition. This is an approximate treatment, as we stated in the Introduction. A separate study, focused specifically on the processes (14-15) and accurate calculations of σ_i^{stab} and σ_i^{diss} for individual resonances of different isotopomers, is planned at the next round of theory development.

Assuming steady-state conditions for concentration of each state $S_2^{(i)}$, allows deriving analytic expression for third-order recombination rate coefficient of the overall recombination process (Babikov et al., 2003b, Pack and Walker, 2004, Grebenshchikov and Schinke, 2009, Ivanov and Babikov, 2016):

$$\kappa_{ET} = \sum_i \frac{\Gamma_i K_{eq}(E_i)}{\Gamma_i + (k_i^{stab} + k_i^{diss})[M]} k_i^{stab}, \quad (17)$$

where the sum is over all scattering resonances $S_2^{(i)}$.

Several processes, less important than (5-8), are neglected in our treatment of energy-transfer kinetics. Namely, we do not include the possibility of back excitations, $S_2 + Ar \rightarrow S_2^{(i)} + Ar$, assuming that concentration of the formed sulfur $[S_2]$ is small. Justification for this is that the equilibrium vapor pressure of S_2 (and larger allotropes) is small, even in the saturated regime over solid sulfur (Lyons, 2008). We also neglect the collision-induced transitions between different scattering resonances, $S_2^{(i)} + Ar \rightarrow S_2^{(j)} + Ar$ assuming that their populations are entirely determined by equilibrium with reagents $S+S$. These assumptions are reasonable at low and moderate pressures of the bath gas.

II-B. Potential Energy Function

Calculations of bound ro-vibrational states (below dissociation threshold) and scattering resonances (above threshold) require the potential energy function $V_{pot}(r)$, where r is the distance between S atoms in S_2 molecule. We computed this function for the electronic ground state $^3\Sigma_g^-$ of S_2 that correlates asymptotically with two ground state ^3P sulfur atoms. Forty five points were computed in the range $1.2 \leq r \leq 12 \text{ \AA}$. Density of points was higher near the bottom of the well, where $V_{pot}(r)$ makes a sharp turn, as shown in Fig. 1a. One-dimensional cubic spline of these *ab initio* data was constructed to obtain smooth function for calculations of the ro-vibrational states. Electronic excited states of S_2 (e.g., $B^3\Sigma_u^-$) are not expected to participate in the process, since thermal energy is not sufficient to reach these states, and also because these states correlate with the excited sulfur atoms (in the ^1D state), but those are quickly quenched by bath gas collisions at ambient pressure.

These *ab initio* calculations were carried out using MOLPRO suite of the electronic structure codes. The choice of theory level and the basis set size were made based on the earlier calculations for S₃ by others (Francisco et al., 2005, Peterson et al., 2006), and our own previous calculations for O₃ (Ayoubz and Babikov, 2012, 2013), that is isoelectronic with S₃. The multi-reference nature of electronic wave function in the asymptotic region requires employment of MRCI theory with Davidson correction (+Q) and large basis set AUG-CC-PV(5+d)Z. In these calculations the equilibrium distance of S₂ was found to be $r_e = 1.899 \text{ \AA}$, in good agreement with literature value of $1.889 \text{ \AA}$ (Herzberg, 1950, and Huber and Herzberg, 1979). The well depth of S₂ was found to be $D_e = 35293 \text{ cm}^{-1}$. Accounting for zero-point energy (see below) gives dissociation energy of $D_0 = 100.56 \text{ kcal/mol}$, in excellent agreement with thermochemical data available from literature: 100.76 kcal/mol (Huber and Herzberg, 1979, Peterson et al., 2006). Thus, we conclude that globally (up to dissociation limit) our potential energy function is chemically accurate.

To obtain another measure of accuracy of the potential, we computed (as explained in the next section) the ro-vibrational states of S₂ and fitted the lower part of obtained spectrum using the standard formula:

$$E(v, j) = \omega(v + \frac{1}{2}) + B j(j+1) - \delta(v + \frac{1}{2})^2 - D j^2(j+1)^2. \quad (18)$$

For ³²S³²S the fit of 27 ro-vibrational states in the lower 2000 cm^{-1} of the spectrum (that included three lower vibrational states $v = 0, 1$ and 2 , and some of their corresponding rotational states up to $j = 40$) gave the following spectroscopic parameters for the vibrational: $\omega = 718.93 \text{ cm}^{-1}$, $\delta = 3.012 \text{ cm}^{-1}$, and rotational components: $B = 0.2900 \text{ cm}^{-1}$, $D = 1.94 \times 10^{-7} \text{ cm}^{-1}$, with standard deviation of the fit $\sim 0.79 \text{ cm}^{-1}$. These are in good agreement with data available from classic literature (Herzberg, 1950, and Huber and Herzberg, 1979): $\omega = 725.65 \text{ cm}^{-1}$, $\delta = 2.844 \text{ cm}^{-1}$, $B = 0.2954 \text{ cm}^{-1}$ and $D = 1.90 \times 10^{-7} \text{ cm}^{-1}$. The difference is largest for harmonic frequency, but note that some experimental measurements give the frequency of S₂ near $\omega = 715 \text{ cm}^{-1}$ (see Eckert and Steudel, 2003, and references there in), so, our prediction is close to the middle of the interval. Furthermore, it is in excellent agreement with $\omega = 720.3 \text{ cm}^{-1}$ computed by Peterson et al., 2006, and with recommendation of Eckert and Steudel, 2003, based

on more recent experimental measurements: $\omega = 720 \text{ cm}^{-1}$. Thus we conclude that in the well region our potential energy function is spectroscopically accurate.

II-C. Energies, Widths and Wave Functions of Resonances

When we speak about ro-vibrational states of molecules we often tend to group multiple rotational states and associate them with a given vibrational state, mostly based on energy considerations (vibrational quanta are much larger than typical rotational excitations). This is convenient in spectroscopy, in experiment, but in theoretical and computational methods we have to reverse the logics. In order to compute ro-vibrational states of a molecule we first assume that the molecule is in a given rotational state j , which creates centrifugal potential $V_{\text{rot}}(r) = j(j+1)/(2\mu r^2)$, where μ is reduced mass of the molecule (in our case S_2) while r is, again, the interatomic distance. This analytic function, reversely proportional to r^2 , gives rotational energy of the molecule (always positive, see Fig. 1a), as a function of the atom-atom distance r , and is added to the potential energy of the molecule (negative) to give the total effective energy $V_{\text{pot}}(r) + V_{\text{rot}}(r)$. Such centrifugally distorted potential is presented in Fig. 1b (for $^{32}\text{S}^{32}\text{S}$ in the rotational state $j = 50$). It exhibits a maximum point, because at small r we usually have $V_{\text{rot}}(r) < |V_{\text{pot}}(r)|$, while in the asymptotic range of large r this is typically opposite: $V_{\text{rot}}(r) > |V_{\text{pot}}(r)|$. This switch is responsible for appearance of centrifugal barrier. In what follows we will characterize centrifugal barrier by position of its top, r^* , and the energy at the top, $E^* = V_{\text{pot}}(r^*) + V_{\text{rot}}(r^*)$, which is the barrier height.

For example, for $^{32}\text{S}^{32}\text{S}$ calculations with $j = 10$ the centrifugal barrier of only $E^* = 1.1 \text{ cm}^{-1}$ is located at $r^* = 18.4 \text{ Bohr}$. When angular momentum is increased to $j = 50$ the centrifugal barrier is $E^* = 65 \text{ cm}^{-1}$, and is found near $r^* = 10 \text{ Bohr}$ (see Fig. 1b). Finally, for $j = 100$ the barrier is $E^* = 412 \text{ cm}^{-1}$ at $r^* = 8.2 \text{ Bohr}$. These numbers give good idea about the range of values in the problem, and can be compared to thermal (kinetic) energy of colliding sulfur atoms which, at room temperature, is close to $\sim 200 \text{ cm}^{-1}$. Roughly, Boltzman population is non-negligible at energies up to $3kT$, which is on the order of $\sim 600 \text{ cm}^{-1}$ for this problem, and requires including rotational states up to at least $j = 120$. To obtain converged results we included all rotational excitations up to $j = 180$, when the height of centrifugal barrier is on the order of

1000 cm⁻¹. Note that even this value is much smaller than the well depth on the potential energy surface, which is on the order of 35000 cm⁻¹ for S₂ (contrast Fig. 1b vs. Fig. 1a). However, it should be understood that the well depth (*below* dissociation threshold) is not directly relevant to the recombination process, since recombination proceeds at thermal energies *above* dissociation threshold.

The next step is to compute energies E_i and wave functions ψ_i for all vibrational states (of each rotational state j) by solving Schrodinger equation $\hat{H}\psi_i(r) = E_i\psi_i(r)$ with the following Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V_{\text{rot}}(r) + V_{\text{pot}}(r) + V_{\text{CAP}}(r). \quad (19)$$

Based on the value of energy, and properties of the wave function, these states can be classified as belonging to one of the following two categories: If energy of the computed state is below dissociation threshold, $E_i < 0$, then this state is stable. It has no enough energy to dissociate (*e.g.*, onto S + S) and is called the *bound* ro-vibrational state of S₂. States at energies above dissociation threshold, $E_i > 0$, are not stable. They can decay onto S + S (dissociate, since they have enough energy for this) and be populated again by S + S collisions at energy E_i . These are *scattering* states, since the process of scattering of two atoms proceeds through these states: S + S → S₂^{*} → S + S. The lifetime of such S₂^{*} state is reversely proportional to its decay rate. One way to look at this is to say that in quantum mechanics, due to uncertainty principle, the lifetime of unstable state is reversely proportional to its width Γ_i (measured in the same units as state energy, here wavenumbers, cm⁻¹). Alternatively, one could look at the time delay for S + S scattering, which tells us how much time the atoms spend together, as unstable molecule S₂^{*}. If time delay is analyzed as a function of collision energy (which is continuous at $E_i > 0$) we would see peaks near some energies E_i , that correspond to longer lived S₂^{*} states. Such conditions are said to correspond to *scattering resonances*. The widths of these peaks would give their decay rates.

In practice, both bound states and scattering resonances for a molecule can be computed simultaneously by introducing complex absorbing potential $V_{\text{CAP}}(r)$ into the asymptotic region

of r as indicated in Eq. (19). It absorbs “tails” of delocalized scattering wave functions, but also makes energies complex-valued (non-Hermitian), say $\varepsilon = E - i\Gamma/2$. Recall that in quantum mechanics time-evolution of wave function for an eigenstate is given by $e^{-i\varepsilon t/\hbar}$. Substitution of complex ε leads to $e^{-iEt/\hbar} \times e^{-(\Gamma/\hbar)(t/2)}$, where first factor gives usual unitary evolution (due to the real part of energy), while second factor describes decay of the state (due to the imaginary part of energy). Square of this expression gives time-evolution of probability, $e^{-(\Gamma/\hbar)t}$, which reveals that the first-order decay rate coefficient is $\Gamma/\hbar$. We often use atomic units, where $\hbar=1$, then Γ is the decay rate, but in principle any units of energy can be used (here wavenumbers, cm^{-1}).

II-D. Technicalities

For numerical solution of Schrödinger equation, we employed the discrete variable representation approach (DVR) with a grid of non-equidistant points generated using the local value of deBroglie wave length, in order to reflect the shape of ro-vibrational potential $V_{\text{rot}} + V_{\text{pot}}$ (Kokoouline et al., 1999, Borisov, 2001, Ivanov and Babikov, 2011, Teplukhin and Babikov, 2016). Such optimized grid has more points over the deep well (which allows describing fast oscillations of wave function there) and fewer points asymptotically, where wave function is smooth (which permits covering a broad range of r). In all calculations reported here the grid of 750 non-equidistant points was used, which extends well beyond 100 Bohr.

Complex absorbing potential $V_{\text{CA}}(r)$ was placed in the asymptotic region, at 40.00 Bohr. Complex eigenvalues $E - i\Gamma/2$ and corresponding wave functions of the DVR matrix were computed using LAPACK package (Anderson et al., 1999). Typically, at energies above threshold, diagonalization produces a mix of the true molecular states (scattering resonances) and the artificial “particle in the box” states. Resonances are easy to recognize by large probability in the well region of the PES, determined by integrating modulus squared of the wave function $\psi_i(r)$ through the range from small values $r \approx 0$ to the centrifugal barrier $r = r^{\ddagger}$. For majority of resonances $S_2^{(i)}$ (narrow resonances localized behind the barrier), the well probability is close to one, $p_w \approx 1$, although some resonances at energies near the top of the barrier and above are

more delocalized and show smaller well probability. We took into consideration all resonances with $p_w > 0.001$.

For calculations of resonance widths Γ_i we tried two different analytic forms of the CAP, one suggested by Balint-Kurti, 1993, and another suggested by Monolopoulos, 2002. We checked and found that, given enough flexibility, one can obtain nearly identical converged widths Γ_i of resonances using these two absorbing potentials. In both cases the required length L of the CAP is determined by a characteristic deBroglie wavelength of the problem λ . However, the CAP of Monolopoulos is built to work for all energies above some chosen minimal value of energy (which is convenient when the spectrum is unknown), while the CAP of Balint-Kurti is optimized to work best for one chosen value of E_i (initially unknown), which seems to be less general. Still, we found a very efficient and automated way to implement the approach of Balint-Kurti in our case. Namely, we noticed that the important scattering resonances are found only near the top of centrifugal barrier. Thus, we can use the barrier height $E^\ddagger$ to generate an individual optimal CAP for each calculation, even though the calculations have to be done repeatedly for many isotopic compositions and for many values of j , and all together span a rather broad range of energies E_i . Thus, we have finally chosen to use the CAP of Balint-Kurti:

$$V_{\text{CAP}}(r - r_{\text{CAP}}) = -iN \times A \exp\left\{-2\frac{L}{r}\right\}, \quad (20)$$

with rather large damping length of six deBroglie wavelengths, $L = 6\lambda$, and the damping strength of $A = 1.77E$ recommended for this damping length, where $E = E^\ddagger$ is the height of centrifugal barrier (which depends on μ and j), while λ is its corresponding deBroglie wavelength, $N = 13.22$ is normalization coefficient. The point where the CAP starts was $r_{\text{CAP}} = 40.0$ Bohr. The value of damping length varies from almost 77 Bohr (for small j) to only 1.7 Bohr for large j .

II-E. Analytic Model for Resonance Widths

In order to run an independent test of our numerically computed widths Γ_i , we also computed the analytic decay rates through a parabolic barrier (Skodji and Truhlar, 1981, and Bowman and Wang, 2016):

$$\Gamma_i(\text{cm}^{-1}) = \frac{\sqrt{2\mu E_i} / h}{1 + \exp\left\{-2\pi \frac{\delta E}{\hbar\omega}\right\}}. \quad (21)$$

Numerator in Eq. (21) is simply a wavenumber of dissociation products for the resonant state at energy E_i . The rest in this equation is probability of transmission through the barrier described by inverted parabola of frequency ω . The meaning of δE is energy of resonance relative to the top of the barrier: $\delta E = E_i - E^\ddagger$ (see Fig. 1b). It is negative for tunneling (under the barrier) and is positive for “slowing” over the barrier. Note that the case of resonance sitting exactly at the top of the barrier, $\delta E = 0$, gives transmission probability of $1/2$. This model was implemented by fitting a parabola to the top of centrifugal barrier (which gives ω) and applying it to numerically computed resonances at energies E_i .

III. Results and Analysis

In this section we report properties of individual resonances for one isotopomer, $^{32}\text{S}^{32}\text{S}$, then we analyze their importance for the recombination process. Isotope effects are discussed in the next section.

III-A. Properties of Individual Resonances

The masses of S atoms are rather large, and the well of S_2 potential is rather deep. It is able to support 82 vibrational states: $v = 0$ to $v = 81$ (for $^{32}\text{S}^{32}\text{S}$ in state $j = 0$). All these are bound vibrational states of S_2 , with energies below dissociation threshold, $E_i < 0$. The effect of rotation, $j > 0$, is demonstrated in Fig. 1b-c. Centrifugal lift raises energies of these states, pushing upper vibrational states into the range above dissociation threshold, $E_i > 0$, where they become scattering resonances. At the same time, the centrifugal barrier is created, which keeps these states localized within the well region. However, the height of the barrier is smaller than the centrifugal lift of the bound states, simply because $r_e < r^\ddagger$ while the rotational potential decreases as $\sim 1/r^2$. Thus, for $j > 0$ the number of vibrational states, including resonances, is always smaller than that in the case of $j = 0$. For example, for the case of $j = 50$ presented in Fig. 1c, we see a centrifugal barrier of about $E^\ddagger = 65 \text{ cm}^{-1}$. In this case the vibrational states up to $v =$

74 are still bound ($E_i < 0$), while the states $\nu = 75$ and $\nu = 76$ become scattering resonances ($E_i > 0$). Higher vibrational states disappear in the continuum.

Note that state, $\nu = 75$ of $j = 50$ at $E_i = 37.2 \text{ cm}^{-1}$ is trapped deep and behind the centrifugal barrier, its width Γ_i is negligibly small, whereas its wave function looks similar to wave function of a bound vibrational state (entirely localized in the well, with no amplitude outside of centrifugal barrier, see Fig. 1c). For such states the tunneling through the barrier is inefficient, which makes formation of S_2^* from (and decay to) $S + S$ impossible. Such states can't contribute to the recombination process.

However, the last state $\nu = 76$ of $j = 50$ at $E_i = 61.0 \text{ cm}^{-1}$ is just a few wavenumbers below the top of centrifugal barrier, and its width is substantial, $\Gamma_i = 0.18 \text{ cm}^{-1}$. Let's analyze wave function of this state, going from right to left (see Fig. 1c). In the asymptotic range ($r \sim 50$ Bohr) this wave function looks like a plane wave that corresponds to the system impinging onto the barrier from right, with kinetic energy E_i and mass μ , which is the reduced mass of $S + S$ collision. Closer to the barrier ($r \sim 20$ Bohr) the frequency of wave function oscillations decreases, which means that the system slows down, climbing the centrifugal potential. Near the top of the barrier ($r \sim 10$ Bohr) oscillations vanish, which means that the system stops, and starts tunneling into the well region. Inside the barrier ($r < 10$ Bohr) the system falls into the deep well, where its wave function represents a highly excited vibrational state of S_2 . This process corresponds to population of the metastable S_2^* from $S + S$ collision.

The scenario discussed above and depicted in Fig. 1c is very typical to S_2 molecule. Usually, for one given value of $j > 0$, we find only one vibrational state with energy E_i near the top of the barrier $E^\ddagger$ that exhibits significant width Γ_i and thus is expected to be important for the recombination process. In rare cases we see two such vibrational states for one j , but not more. To demonstrate this, we collected all scattering resonances of S_2 computed for a broad range of rotational excitations, $8 \leq j \leq 180$, and plotted their widths all together in Fig. 2, in a broad range of values $10^{-5} \leq \Gamma_i \leq 10^2 \text{ cm}^{-1}$. Figure 2a gives the dependence on j ; resonances that correspond to the same vibrational state ν are connected by lines for convenience. We see that for each vibrational state the width of resonance grows exponentially fast as we increase j . This

is because rotational excitation lifts resonances closer to the top of centrifugal barrier. Near the top of the barrier resonances exhibit widths between $\Gamma_i \sim 1 \text{ cm}^{-1}$ (near $j \sim 10$) and $\Gamma_i \sim 10 \text{ cm}^{-1}$ (near $j \sim 110$). Further increase of rotational excitation leads to disappearance of the upper vibrational state, and its replacement by the next (lower vibrational) state. Thus, at low $j \sim 10$ only state $v = 81$ has non-negligible width. Near $j \sim 20$ state $v = 80$ dominates. Close to $j \sim 30$ it is replaced by $v = 79$, etc., down to the state $v = 67$ that becomes important at $j \sim 120$.

Figure 2b shows widths of the same resonances as in Fig. 2a (all $8 \leq j \leq 180$ together) but now as a function of energy of the resonance with respect to the top of the barrier, δE . We see that broadest resonances are, indeed, found at energies near and above the barrier top, $\delta E \geq 0$. No resonances are found at energies beyond $\delta E = 20 \text{ cm}^{-1}$ above the top. Below the top of the barrier (in the tunneling regime) the widths decrease roughly exponentially as a function of δE , but somewhat differently for different values of v and j . Resonances trapped deeper than $\delta E = -100 \text{ cm}^{-1}$ (far below the barrier top) exhibit smaller widths and can be safely ignored.

Figure 3 demonstrates the test of analytic model for calculations of resonance widths, Eq. (21). As before, resonances in $^{32}\text{S}^{32}\text{S}$ for the entire range $8 \leq j \leq 180$ are plotted together. An impressive six orders of magnitude range of values $3 \times 10^{-5} \leq \Gamma_i \leq 30 \text{ cm}^{-1}$ is shown. The model is found to work well globally, although near $\Gamma_i \sim 1 \text{ cm}^{-1}$, most important for the recombination process, it slightly overestimates the values of Γ_i . But the model is more accurate for both higher and lower widths, near $\Gamma_i \sim 10^{-2} \text{ cm}^{-1}$ and near $\Gamma_i \sim 10 \text{ cm}^{-1}$. Thus, we conclude that this analytic model can be used for semi-quantitative prediction, which is often our goal, including this paper. It also gives extra-confidence in our numerical results.

III-B. Contributions to Recombination

Equation (17) gives the total recombination rate coefficient as a sum over all resonances in the molecule, $\kappa = \sum \kappa_i$, but it is instructive to know the distribution of κ_i values before summing them up. In Figure 4 we plotted individual contributions κ_i (at room temperature and atmospheric pressure of bath gas) of all ro-vibrational resonances computed for in $^{32}\text{S}^{32}\text{S}$ for the range $8 \leq j \leq 180$. Upper frame shows these data as a function of j . For $j < 8$ the system has no centrifugal barrier, and no resonances. For $j > 180$ the barrier is so high that the Boltzman factor

shuts off the reaction (see Eq. (A1) in Appendix A). Within this range of rotational excitations, several different vibrational states contribute to the process, as we discussed above. Interestingly, Fig. 4 shows that the number of non-negligible contributions is very manageable. It appears that about 100 individual ro-vibrational resonances make non-negligible contributions to the process. The largest contributions come from rotational excitations in the range $50 \leq j \leq 60$ (and vibrational states near $v = 75$ or 76), but the overall distribution is rather broad.

Middle frame in Fig. 4 gives individual contributions of resonances κ_i plotted as a function of their width Γ_i (that reflect their decay rates). This allows seeing that the widths of resonances, that make the most important contribution to recombination, range from $\Gamma_i \sim 3 \times 10^{-3} \text{ cm}^{-1}$ to $\sim 20 \text{ cm}^{-1}$. Again, the distribution is rather broad, with maximum near $\Gamma_i \sim 3-4 \text{ cm}^{-1}$. Lower frame in Fig. 4 gives κ_i as a function of δE , which demonstrates that largest contributions to recombination come from resonances formed near the top of centrifugal barrier, in the energy range between $\delta E = -40 \text{ cm}^{-1}$ and $+10 \text{ cm}^{-1}$.

Summation of contributions of all resonances, Eq. (17), gives the following value for the rate coefficient of recombination: $\kappa_{\text{ET}} = 1.22 \times 10^{-33} \text{ cm}^6/\text{s}$ (including odd j values only). Note that this number is about one half of the experimental value given in the Introduction. This is OK, since it only gives contribution of the energy-transfer mechanism. The chaperon mechanism and the three-body contributions should be computed separately and added to it. And, at this point the absolute value is not as important as the relative value of the isotope effect (discussed below).

If the analytic model of Eq. (21) is used for resonance widths (instead of numerically determined values of Γ_i), the predicted rate coefficient for recombination is found to be $\kappa_{\text{ET}} = 1.27 \times 10^{-33} \text{ cm}^6/\text{s}$, just slightly above the accurately computed coefficient, consistent with our earlier observation that the model slightly overestimates the values of Γ_i . This reasonably accurate result opens up practical possibility for an approximate treatment of the recombination process (for the problems where the above mentioned accuracy is sufficient). Namely, if the values of Γ_i can be predicted analytically, then we don't really have to use the CAP, or solve the complex-eigenvalue problem. Moreover, the range of the grid can be reduced dramatically, to only include the well region, up to the location of the top of the barrier $r = r^\ddagger$. In such set up the

quasi-bound vibrational states at energies up to the barrier top $E_i = E^*$ (plus, may be, one more state) are computed by solving Schrodinger equation with *real-valued* potential, for various values of j , and those energies E_i are then fed into the analytic expression of Eq. (21), to predict the values of Γ_i . This is a much simpler (but approximate) procedure that may be sufficient in some cases.

Given success of the analytic model for resonance width, we decided to build a simplified model for the entire recombination process. Namely, instead of using the numerically computed values of resonance energies E_i , we can assume that at any value of j there is only one dominant resonance, sitting right at the top of centrifugal barrier, $E_i = E^*$. For such resonances the barrier transition probability is $1/2$. Resonance width is determined only by the numerator in Eq. (21) and depends on rotational excitation (and the reduced mass): $\Gamma(j) = \sqrt{\mu E^* / 2} / h$. The resultant rate coefficient is $\kappa_{\text{ET}} = 1.77 \times 10^{-33} \text{ cm}^6/\text{s}$, which is a factor of 1.5 larger than the accurately computed value, but is still smaller than the experimental value, or the value used in the kinetics model (see Introduction). This approach is practical, since now we don't have to solve the Schrodinger equation at all. All we have to do is to determine the energy of centrifugal barrier top for each j (numerically, as we did here, or even analytically). The reason why the rate coefficient predicted in this way is larger than the accurately computed one is also clear. From Figs. 2 and 3 one can see that resonances are not always at the top of the barrier, but only once in a while. So, placing the resonance at the barrier top for every j must lead to overestimation of the rate, and this is exactly what we see. In a situation when the reason for deviation of the model is clear, it is safe to introduce an empirical scaling factor to make the model quantitatively accurate.

All results presented so far (Figs. 4 and the values of recombination rate coefficients) correspond to the simplest possible way of describing stabilization step of the recombination process, in which one single value of stabilization cross section $\sigma^{\text{stab}} = \sigma_0$ is used for all scattering resonances, independent of their energy, character or ro-vibrational content (as explained in Sec. II). We did this intentionally, to have a clear picture of the effect of resonance properties, energy and width on the recombination rate coefficient, unobscured by any other factors such as stabilization cross section. But now it's a time to take into account the fact that

some resonances, particularly those close to the barrier top, exhibit a significant amplitude outside of the well (e.g., state $v = 76$ in Fig. 1c). Efficiency of their stabilization (by third body collision) to stable S_2 is smaller, compared to those cases when the wave function is localized entirely in the well (e.g., state $v = 75$ in Fig. 1c). In order to take this effect into account we should scale down stabilization cross sections for delocalized states.

In principle, one could use for this the value of well probability, $p_w \leq 1$, as a scaling factor, namely: $\sigma^{\text{stab}} = \sigma_0 \times p_w$. However, the value of p_w depends on position of the CAP, and is thus somewhat arbitrary, although it is correct qualitatively. Another suitable and better defined moiety in our theory is the value of transition probability from Eq. (21): $p_t = 1/(1 + \exp\{-2\pi\delta E/(\hbar\omega)\})$. This can be computed analytically for each resonance, and the value of stabilization cross section for each resonance can be scaled down accordingly: $\sigma^{\text{stab}} = \sigma_0 \times (1 - p_t)$. For a resonance sitting right at the top of the barrier this approach gives $\sigma^{\text{stab}} = \frac{1}{2}\sigma_0$. In any case, one should have in mind that whatever method is used, the value of recombination rate coefficient will be reduced. For example, if we adopt the p_t scaling, and compute the rate using the numerically accurate energies E_i and widths Γ_i of resonances, we obtain $\kappa_{\text{ET}} = 0.67 \times 10^{-33} \text{ cm}^6/\text{s}$; if we use analytic model for the widths, keeping accurate resonance energies E_i , we obtain $\kappa_{\text{ET}} = 0.73 \times 10^{-33} \text{ cm}^6/\text{s}$; finally, the “resonance-at-the-top” model for the entire recombination process gives us $\kappa_{\text{ET}} = 0.90 \times 10^{-33} \text{ cm}^6/\text{s}$.

This trend is similar to what we saw above, with model predictions being again higher than the accurately computed values. It should also be noted that results of Fig. 4 would change with this modification. Updated version is given in Fig. 5, and we see that if delocalization or resonances is taken into account the largest contributions to recombination come from rotational excitations around $j \sim 60$ (small change compared to Fig. 3). Most important resonances exhibit widths in the range $\Gamma_i \sim 0.3\text{--}0.4 \text{ cm}^{-1}$ and are found typically below the barrier top, near $\delta E = -5 \text{ cm}^{-1}$. Overall, the distributions of Fig. 5 are somewhat narrower than those in Fig. 4. They die off faster at the higher end of the range.

IV. Discussion

IV-A. Mass Dependence

We start the discussion of isotope effects by reporting results of a theoretical/computational experiment, in which the mass of one sulfur atom remains equal to that of ^{32}S , while the mass of the second S atom in S_2 molecule is changed quasi-continuously (by very small increments) through the range from exactly 32 amu, to exactly 36 amu. Through this experiment the value of recombination rate coefficient κ_{ET} is computed using the methods discussed above. Note that here we do not exclude from consideration the rotational states with even values of j , to have a consistent picture through the entire range of masses. Also note that the reduced mass of $^{34}\text{S}^{34}\text{S}$ is just slightly outside of the range covered by this computational experiment. The physically meaningful predictions, relevant to the naturally occurring S_2 molecules, are given at the end of Section IV.

Figure 6a presents results of calculations using the simplest model for stabilization step, with constant cross section $\sigma^{\text{stab}} = \sigma_0$. These data show large isotope effect, with complicated mass dependence. Overall, the value of κ_{ET} tends to decrease as the mass is raised, but on top of that we see rather frequent irregular oscillations, with rather large amplitudes. To quantify this “zigzag” behavior we fitted the data in Fig. 6a by a straight line $\kappa = \kappa_0 - \alpha m$, which gave $\kappa_0 = 3.11$ and $\alpha = 0.0208$ with standard deviation of the fit 0.0302 (all in the units of Fig. 6). From these numbers we can deduce that on average the recombination rate coefficient drops by 3.4% as the mass of S atom is raised from 32 to 36 amu, which by itself is a significant effect. But the amplitudes of “zigzag” are often even larger (see Fig. 6).

This striking finding was in contrast with our expectations. Initially we thought to find smooth dependencies and small isotope effects, since mass differences of sulfur isotopes are rather small relative to their absolute values (at least when one attempts to draw parallels with hydrogen isotopes). The sharp features of Fig. 6a have to be understood. Can it be that this is an artifact of calculations? Or, a drawback of the model? Or, this behavior is real and should be found in the naturally occurring molecules?

Figure 6b shows in detail a fragment (from 32.4 to 32.8 amu) of the dependence given in Fig. 6a. Several elements of “zigzag” are clearly seen. Let’s focus on one monotonic piece of this dependence, in even smaller range of masses from about 32.57 to about 32.61 amu (eight points

in the green range in Fig. 6b). Detailed analysis of resonance spectra shows that in this range of masses the spectra contain exactly the same resonances, as labeled by rotational and vibrational quantum numbers ν and j . Their energies and lifetimes depend on the value of reduced mass as follows: Increase of the mass leads to decrease of state energies E_i , which in turn decreases the values of resonance widths Γ_i , because resonances are shifted down, further from the top of centrifugal barrier, thus, they have to tunnel through the increasingly large barrier. This reduction of resonance widths leads to decrease of the recombination rate coefficient κ , according to Eq. (17), and the effect is pretty sharp, since resonance width depends exponentially on δE , according to Eq. (21). From Fig. 6b we estimated that the slope of this segment (green range) is larger than the overall trend (red dashed line) by a factor over 200. This clearly means that even small mass change, in this example by only 0.04 amu, has very large effect on contribution of individual resonances. The dependence is negative, very fast, and within a short range of masses is monotonic (e.g., through the green range in Fig. 6b).

However, this monotonic behavior stops near the mass value of 32.61 amu, where the rate coefficient receives a sudden boost, making a “zigzag”. Analysis of the resonance spectra shows that starting at the mass of about 32.61 amu, one more resonance shows up in the spectrum: $j = 50$, $\nu = 77$. Indeed, decrease of the mass, at some point, permits to fit one more state behind the centrifugal barrier, in the vicinity of its top (see Fig. 9 below). Such resonances are typically broad, and make very substantial contributions to recombination. Analysis of every “zigzag” in Fig. 6b shows that each sudden boost of the rate coefficient is due to appearance of one, sometimes two new resonances in the spectrum. Several typical cases are indicated in Fig. 6b. Overall, in the range from 32 to 36 amu in Fig. 6a, there are about 130 pronounced “zigzag” features, due to involvement of new ro-vibrational resonant states of S_2 molecule.

While the appearance of new ro-vibrational states in the spectrum is a real physical process, the “zigzag” behavior of the rate coefficient is, most probably, a drawback of the present model, where stabilization of scattering resonances is treated approximately, using one constant value of cross section $\sigma^{\text{stab}} = \sigma_0$ for all resonances. The problem comes from those new resonances that just joined the recombination process (due to the mass increase, as explained above). Typically, such resonances (near the top of the barrier) exhibit rather delocalized wave functions. Probability to find the system inside of the barrier is small, which should also reduce

its stabilization probability. One can say that resonances with larger widths should have smaller stabilization cross section, while narrower resonances should have larger stabilization cross sections. Allowing broad resonances to have large stabilization cross sections is unphysical and leads to appearance of zigzags as in Fig. 6.

In order to fix this problem rigorously one has to compute stabilization cross sections accurately, for each individual resonance, which goes far beyond the goals of present paper. But here we can try to apply a more realistic stabilization model, either $\sigma^{\text{stab}} = \sigma_0 \times p_w$ or $\sigma^{\text{stab}} = \sigma_0 \times (1 - p_t)$, in order to mimic the actual effect by reducing the value of stabilization cross section for broad resonances, accordingly to delocalization of their wave functions. We tried both expressions. Results are presented in Fig. 7. The values of rate coefficient are smaller, due to reduction of stabilization cross section. In the case of p_t -scaling the overall trend can be described by a linear fit with $\kappa_0 = 1.82$, $\alpha = 0.0137$ and standard deviation of only 0.006 (same units). In this case the rate coefficient decreases by about 3.9% (when the mass increases from 32 to 36 amu), similar to what we saw without any scaling of cross section. However, the amplitudes of zigzags are much smaller now, roughly by a factor of 10, and are barely distinguishable in Fig. 7. In the case of p_w -scaling the overall trend is described by a linear fit with $\kappa_0 = 1.00$, $\alpha = 0.00685$ and standard deviation of only 0.0005 (same units). Here the rate coefficient drops by about 3.5% (for the mass increase from 32 to 36 amu) which, again, is very close to the unscaled result, but now zigzags vanish completely (indistinguishable in Fig. 7). It seems to us that such smooth dependence is physically correct, in contrast to the irregular dependence of Fig. 6, which is likely to be largely artificial.

We will discuss consequences of this interesting property further below. Here we would like to mention briefly that at the review stage of this paper it was brought to our attention that similar effect was observed in the computational studies of S-MIF produced by chemisorption reactions (Lasaga et al., 2008; Balan et al., 2009). It was assumed that a sulfur-containing molecule is adsorbed to a surface by shallow attractive potential (Morse model), that can support a finite number of bound vibrational states. Raising the mass of sulfur isotope makes the spectrum denser, and allows fitting one more bound state into the same well. This translates into more bound states and larger values of partition function, for heavier isotopes. Initially, it was

argued (Lasaga et al., 2008) that this effect could lead to MIF of sulfur since, within statistical approach, fractionation is given directly by the ratio of partition functions for two isotopic cases. However, a year later it was demonstrated (Balan et al., 2009) that this effect is artificial. It happens only when all the scattering states at $E_i > 0$ are completely neglected. If they are included, the isotope effect is smooth and mass dependent! A “sharp cut” of the spectrum at $E_i = 0$ was responsible for mass-independent effect, which is indeed similar to what we see here. The difference is that we deal with rotation that creates many more states (on the order of a hundred, rather than one extra state), we accurately compute them (including decay rates), we do not cut-off any states, and we recognize that a smooth, physical dependence for stabilization cross section must be incorporated into the model for higher energy resonances.

IV-B. Analytic Model

For methodological purpose we tested the analytic model for resonance widths, Eq. (21), by applying it to the range of masses from 32 to 36 amu. The results were very similar to those reported above: significant “zigzags” are present only if we use a constant stabilization cross section, but they vanish if cross sections are scaled. Also, we tested the analytic resonance-at-the-top model for the entire recombination process. Note that in this approach, by construct, the number of resonances does not change when the mass of the system is raised, which automatically eliminates the possibility of “zigzags”! The mass dependence is completely smooth and monotonic through the entire range (see Fig. 7). Importantly, the isotope effect is still similar to the numerically accurate case, and is 3.7% decrease of the rate coefficient if the mass is raised from 32 to 36 amu.

One important application of the analytic model is that it can help us to understand the negative mass dependence of the recombination rate coefficient κ in Figs. 6 and 7. Figure 8 presents the dependence of κ_i on j obtained using the analytic model (including scaling of stabilization cross section) for the left-most and right-most points of the dependence in Fig 7, that roughly correspond to $^{32}\text{S}^{32}\text{S}$ and $^{32}\text{S}^{36}\text{S}$ isotopic compositions. The analytic dependence in Fig. 8 is very smooth and easy to analyze, in contrast to the numerically computed results of Figs. 4a and 5a. The total rate $\kappa = \sum \kappa_i$ is computed as a sum over all points in this figure, and now we see where the isotope effect, or mass dependence, comes from, namely: In the range of

rotational excitations $j > 90$ the heavier isotope is formed faster, while in the range $j < 90$ the lighter is formed faster, and this lower- j effect is dominant. The difference for $^{32}\text{S}^{32}\text{S}$ and $^{32}\text{S}^{36}\text{S}$ that we see in Fig. 8 is consistent with 3.7% decrease of the rate coefficient we saw in Fig. 7.

To obtain further insight we collected in Table I the characteristics of resonances in $^{32}\text{S}^{32}\text{S}$ and $^{32}\text{S}^{36}\text{S}$ for two representative values of rotational excitation, $j = 50$ and $j = 120$. Recall that in our analytic model there is only one resonance per j , that sits right at the top of the barrier (these are the points we see in Fig. 8). From Table I we see that although the change of mass m_2 of the second atom is large (12.5%) the difference of reduced masses μ is twice smaller. Its effect on position of centrifugal barrier (in $^{32}\text{S}^{36}\text{S}$ vs $^{32}\text{S}^{32}\text{S}$) is minimal, less than 1%, but its effect on energy of the barrier top E^* (which is also the energy of the resonance E_i in the model) is quite significant, more than 7%. Resonance width Γ_i depends on both resonance energy and the reduced mass, but two effects largely cancel, leading to only $\sim 1\%$ difference in $^{32}\text{S}^{36}\text{S}$ vs $^{32}\text{S}^{32}\text{S}$. It appears that the largest effect comes through equilibrium constant $K_{\text{eq}}(E_i)$ for formation and decay of the resonances (see Appendix A). In Table I we see that for $j = 50$ the heavier isotopomer, when compared to lighter isotopomer, has 6% smaller $K_{\text{eq}}(E_i)$ while for $j = 120$ it has 16% larger $K_{\text{eq}}(E_i)$, and these differences translate directly into the difference of rate coefficients κ_i in Fig. 8. We also checked and found that the entire j dependence of κ_i (seen in Fig. 8) comes dominantly from j dependence of the equilibrium constant $K_{\text{eq}}(E_i)$. But the central question is mass dependence of $K_{\text{eq}}(E_i)$. It comes through two factors: i) Boltzman factor in the numerator of Eq. (A1) that contains energy of the resonance, or the barrier top, that we saw is rather sensitive to the mass (see Table I), and ii) Translational partition function in the numerator of Eq. (A1), see Eq. (A2). We checked and found that near $j = 50$ the first factor has weak positive (+2.4%) mass dependence, $\exp\{-c/\mu\}$, while the second factor has stronger and negative (−8.2%) mass dependence, $\mu^{-3/2}$, which dominates.

To conclude, the overall process is rather involved, with many factors contributing differently in different ranges of parameters, but one dominant factor is an almost trivial (and classical) mass dependence of the translational partition function in the denominator of statistical equilibrium constant.

IV-C. Isotope Effects

Finally, we computed the values of recombination rate coefficients for the major isotopomers of S_2 . Three different versions of theory were used, and the corresponding results are listed in Tables II, III and IV. One should remember that in symmetric (homonuclear) isotopomers only odd rotational states are allowed, such as $j = 1, 3, 5$, etc. For this reason the rate coefficients for $^{32}S^{32}S$ and $^{34}S^{34}S$ are expected to be smaller, roughly by a factor of two, compared to those of $^{32}S^{33}S$, $^{32}S^{34}S$ and $^{32}S^{36}S$. In order to see the trends, we report two sets of data for each isotopomer: computed with all values of j , and with odd j only. The cases that correspond to naturally occurring molecules are underlined in Tables II, III and IV. Namely, for $^{32}S^{33}S$, $^{32}S^{34}S$ and $^{32}S^{36}S$ underlined are the numbers closer to the center of the table (all j included), while for $^{32}S^{32}S$ and $^{34}S^{34}S$ underlined are the numbers closer to the right part of the table (only odd j included). As expected, those are different by, roughly, a factor of two.

Table II summarizes results obtained numerically using the accurately computed energies and widths of resonances, and one constant value of stabilization cross section. We see that although the overall negative mass dependence is still evident, some of the rate coefficients deviate from it significantly. This is due to the zigzag behavior discussed above. The case of $^{32}S^{33}S$ just happens to be closer to the top of a zigzag, while the case of $^{32}S^{36}S$ happens to be closer to the bottom of another zigzag, which makes them deviate from the major trend. Unfortunately, the predictions of Table II are hard to guarantee, because the fine zigzag behavior is rather sensitive to several components of calculations (such as potential energy surface). What we can say for sure is that the effect of individual resonances on rate coefficient of recombination is limited by roughly $\pm 3\%$ of its absolute value. It is always possible to identify individual ro-vibrational states responsible for zigzags (see Fig. 6b), but since the period of zigzags is so small (see Fig. 6a), the effect may almost look accidental. Due to these features, individual resonances may indeed be responsible for mass-independent isotope effects, superimposed with the general negative mass dependence of rate coefficient.

The negative mass dependence becomes evident in Table III that summarizes results obtained numerically (using accurately computed energies and widths of resonances), but now in combination with p_w -scaling of stabilization cross sections, as explained in Sec. III-C. One can see that these data follow the negative mass dependence much better, showing clearly that the

rate coefficient is reduced, by up to $\sim 4\%$, when the mass is raised by isotopic substitutions. Although this dependence is monotonic, one can still see that it is not perfectly smooth. The reason for this is that the overall rate is still the sum over individual quantized resonances, with varying properties. We also see that these remaining irregularities magnify slightly when we remove states with even j values, simply because fewer ro-vibrational states remain, and each individual state matters more. Consistent with Fig. 7, the values of rate coefficients are smaller when stabilization cross sections are scaled down (compare Table III vs Table II). For quantitative description of the effect, accurate values of stabilization cross sections should be computed for individual resonances.

Finally, Table IV gives the data similar to those in Tables II and III, but obtained using the analytic top-of-the-barrier model, where all properties change smoothly. The mass dependent isotope effect is perfectly seen in this case (e.g., close to 4% reduction of rate coefficient in the case of $^{34}\text{S}^{34}\text{S}$ compared to $^{32}\text{S}^{32}\text{S}$). The dependence on mass is monotonic and is perfectly smooth. Also note that the relative effect is nearly identical in the cases when all j are included, and only odd j are included, indicating no difference between symmetric and asymmetric S_2 molecules, beyond the statistical factor of two. We could say that in this example all the mass-independent isotope effects (due to individual quantized states) are removed, and only the mass-dependent classical isotope effect remains.

IV-D. Implications for Early Atmosphere of Earth

As it becomes clear from the previous section, at the current level of theory (without accurate treatment of stabilization cross sections) the mass-independent isotope effects seen in Table II are largely accidental, and should be revised in the future work. However, the mass-dependent effect seems to be robust (same slope of all four curves in Fig. 7), present in all considered cases (Tables II-IV) and is understood in great detail (Sec. IV-B, Fig. 8). Thus, it makes sense to examine what isotope fractionations would result from this effect, which can be done using the data predicted by simplest analytic version of theory, Table IV.

As one of us showed in a recent paper (Babikov, 2017) isotope fractionations due to recombination reaction $\text{S} + \text{S} \rightarrow \text{S}_2$ are given by the following expression:

$$\delta = \frac{\kappa}{2\kappa_s} - 1, \quad (22)$$

where κ_s is the rate coefficient for formation of symmetric $^{32}\text{S}^{32}\text{S}$ (the major non-substituted isotopologue), whereas κ is the rate coefficient for formation of singly substituted asymmetric species: $^{32}\text{S}^{33}\text{S}$, $^{32}\text{S}^{34}\text{S}$ and $^{32}\text{S}^{36}\text{S}$. Each case is considered separately, the doubly substituted $^{34}\text{S}^{34}\text{S}$ is neglected. Using the data of Table IV one obtains: $^{33}\delta = -8.9\text{‰}$, $^{34}\delta = -18.5\text{‰}$ and $^{36}\delta = -36.4\text{‰}$. These give the multiple-isotope fractionation described by $^{33}\Delta = -8.5\text{‰}$ and $^{36}\Delta = +31.3\text{‰}$. On a standard $^{36}\Delta$ vs. $^{33}\Delta$ diagram this would give a point that falls on a curve with the slope of -3.7 (roughly).

The Archean rock record exhibits S-MIF that is characterized by a slope of -1.1 to -1.2 on the $^{36}\Delta$ vs. $^{33}\Delta$ diagram (Kaufman et al, 2007; Ono et al, 2009). It is encouraging that the datum we obtained also shows *negative* slope. But, the magnitude of the slope is off, by a factor of three (at least).

It should be honestly stated that at this point one should not really expect any quantitative agreement. First of all, this is because more accurate treatment of stabilization cross sections is clearly needed, as it was emphasized in Sec. IV-A. Second, as it was outlined in the Introduction, at least the chaperon mechanism (but it even may be that some three-body contribution) should be added to the energy-transfer mechanism studied here. Moreover, as it was emphasized in a recent publication by one of us (Babikov, 2017), the isotopic composition produced by recombination process may be partially or largely scrambled by fast atom exchange reaction (e.g., $^{32}\text{S} + ^{32}\text{S}^{34}\text{S} \rightarrow ^{32}\text{S}^{32}\text{S} + ^{34}\text{S}$). Finally, the products are expected to be diluted by the accompanying atmospheric and sedimentary chemistry. Therefore, the values of fractionations computed and presented in this sections should be regarded as very preliminary, rough estimates.

V. Conclusions

In this paper we presented results of the first (to our best knowledge) theoretical and computational analysis of energy transfer mechanism for recombination of two sulfur atoms into a diatomic molecule, S_2 . This process initiates a series of sulfur polymerization reactions that produce allotropes up to S_8 , and is believed to play important role in the anoxic atmosphere of Archean Earth. The main goal was to understand how much the rate coefficient of this recombination process can be affected by isotopic substitutions, whether these isotope effects are

expected to be mass-dependent or mass-independent, and could they lead, at least potentially, to mass-independent fractionation of sulfur isotopes discovered in the Archean rock record.

At this first exploratory step we adopted a simplified approach, in which we characterized rather accurately everything related to S_2 molecule itself (potential energy function, spectra of rovibartional states, energies and lifetimes of scattering resonances and their wave functions) but, in order to make calculations feasible, we made assumption about stabilization of metastable S_2 by bath gas collisions. Namely, we assigned one stabilization cross section to all scattering resonances, irrespectively of their properties. The value of this cross section was estimated, based on the mixed quantum/classical calculations of rotational energy transfer in $Ar + S_2(j=50, v=0)$ collisions. Since such framework is approximate, our focus was on qualitative understanding of isotope dependencies and on major properties of the process, rather than on predicting the solid numbers.

Nevertheless, the absolute value of recombination rate coefficient that we computed for $^{32}S^{32}S$ at room temperature and atmospheric pressure, $\kappa_{ET} = 1.22 \times 10^{-33} \text{ cm}^6/\text{s}$, came out pretty close to experimental result, $\kappa_{exp} = 2.8 \times 10^{-33} \text{ cm}^6/\text{s}$. One should remember that the experiment is likely to measure the result of all mechanisms of recombination process: the energy-transfer (Lindeman mechanism), the chaperon (radical complex mechanism), and the direct three-body contribution. For comparison, in ozone recombination reaction the contributions of energy transfer and chaperon mechanisms are about equal at room temperature, while the contribution of three-body is only about 5% of the entire rate (consistent with low pressure regime). Thus, our computed rate coefficient is not in contradiction with experimental data, while the value for the direct thee-body contribution reported in the literature, $\kappa_{3B} = 4.19 \times 10^{-33} \text{ cm}^6/\text{s}$, is likely to be somewhat too large. In any way, the agreement within an order of magnitude is well sufficient for the goals of this paper.

We conducted a detailed analysis of properties of individual scattering resonances in S_2 that included distributions of their energies (with respect to the barrier top) and decay rates, their vibrational and rotational content, wave functions, and their individual contributions to the rate coefficient. We found that most important for the recombination process are resonances formed in the narrow energy range near the barrier top. The spectrum of states in S_2 is not very dense.

Typically, there is only one dominant resonance (one vibrational state, ν) for each value of rotational excitation (angular momentum j). For example, in homo-nuclear S_2 , in which only odd j values are allowed, there are only about 50 ro-vibrational resonances that make large contributions to the process.

This finding helped us to develop an approximate analytic model for the recombination process, that happened to be acceptably accurate for description of resonance widths (decay rates), for prediction of the rate coefficients, and even for understanding the mass-dependence of the overall recombination process (the isotope effects). In particular, it was determined that when the properties/contributions of individual quantized resonances are smoothened down or eliminated completely, the mass dependence is governed by statistical translational partition function (denominator of the equilibrium constant). This classical phenomenon leads to a *weak negative mass-dependent isotope effect*. Namely, when the mass of sulfur isotopes is raised from $^{32}S^{32}S$ to $^{34}S^{34}S$ the value of recombination rate coefficient is found to decrease by close to 4%. All other isotopic combinations for sulfur are within this range of masses, and the dependence on mass is smooth.

We also found that on top of this weak effect one can observe another isotope effect that is about 200 times sharper! It is related to mass dependence of contributions from individual quantized resonances. When the mass of the system is raised, energies of resonances decrease (very similar to decrease of vibrational frequency for heavier isotopes), which moves resonances down the spectrum, further away from the top of centrifugal barrier, as shown in Fig. 9. This change reduces the values of resonance widths (exponentially) leading to sharp decrease of the recombination rate. However, at some point the mass decrease is sufficient to free up enough space in the spectrum and fit in one more resonance state (see Fig. 9). When such “new” state shows up in the spectrum, the value of recombination rate receives a sudden boost, since the resonances near the top of the barrier are typically broad and make large contributions. The resultant mass-dependence is characterized as “zigzag” with significant amplitude, up to $\pm 5\%$, and seemingly irregular shape (although it is always possible to analyze each peak and determine the ro-vibrational state responsible for it). The resultant isotope effect is *large, rather irregular and looks mass-independent*, since the mass change due to isotopic substitutions is relatively large, and one isotopomer may happen to be close to the top of a zigzag, while the other isotopomer is closer to the bottom of another zigzag.

While this mass-independent phenomenon was important to catch and its origin was important to identify, it is also important to realize that, most probably, it is exaggerated in our simplified approach. We finally came to a conclusion that amplitudes of zigzags are large only if we use one constant value of stabilization cross section for all resonances (recall that this is the major approximation of our framework). It seems to us that doing so is not quite correct, since the resonances near the top of the barrier (those same resonances responsible for zigzags) must have smaller stabilization cross sections, because their wave functions are rather delocalized, and the probability to find the system in the region behind the centrifugal barrier (where it can be quenched to stable S_2 molecule, by third body collision) must be smaller. This effect would naturally decrease contributions of “new” resonances, leading to smoothening of zigzags.

We tried two methods for scaling down cross section for stabilization of resonances based on delocalization of their wave functions and, indeed, observed that the zigzag behavior became much smoother (or even vanished completely), which led to reduction of the mass-independent isotope effect, and dominance of the mass-dependent classical isotope effect with negative mass dependence. However, the accuracy of this simple fix should not be overemphasized. There is a good chance that in the real S_2 molecules some of the effect of individual quantized resonances still survives, and leads to mass independent isotope fractionations. We believe that the magnitude of this remaining quantum effect is close to what we predicted in this paper, but within the framework of the approximate theory used here it is hard to be more definite.

It becomes clear that more accurate description of the recombination process requires more rigorous treatment of stabilizing $Ar + S_2^*$ collisions. While it is next to impossible to compute stabilization cross section for each individual resonance (in each isotopomer) using the full-quantum approach, it seems to be quite feasible to employ the mixed quantum/classical theory for some typical cases, like resonances near the top of centrifugal barrier, to come out with better prediction of the absolute value of stabilization cross section, and, for example, to map out the dependence of this cross section on energy of the resonance with respect to the barrier top, $\sigma^{\text{stab}} = f(\delta E)$. Such a model would offer a significant improvement over this work, and is something we plan developing in the near future.

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Appendix A: Micro-Canonical Equilibrium Constant

For $S + S \rightleftharpoons S_2^{(i)}$ process, the equilibrium constant for each resonance $S_2^{(i)}$ at energy E_i can be calculated statistically as ratio of partition functions for products and reactants:

$$K_{\text{eq}}(E_i) = \frac{3(2j+1)e^{-E_i/kT}}{Q_{\text{tr}}Q_{\text{el}}}, \quad (\text{A1})$$

Numerator in Eq. (A1) includes degeneracy of the electronic triplet state of S_2 , accounts for space degeneracy of its rotational states, and for thermal population of its ro-vibrational states. Note that since each resonance is considered separately there is no typical symmetry factor of $1/2$ for symmetric species. This effect is taken into account by the sum in Eq. (17). In the cases of $^{32}\text{S}^{32}\text{S}$ or $^{34}\text{S}^{34}\text{S}$, where only odd rotational states are allowed, that sum includes only the allowed states, leading to a factor of $\sim 1/2$ for these homonuclear molecules. Denominator in Eq. (A1) contains the standard partition function for translational states of $S + S$:

$$Q_{\text{tr}} = \left(\frac{\mu_{S+S} k_B T}{2\pi \hbar^2} \right)^{3/2}, \quad (\text{A2})$$

and for the electronic states of two S atoms:

$$Q_{\text{el}} = Q_S^2 = [5 + 3\exp(-396.055 \text{ cm}^{-1}/T) + \exp(-573.640 \text{ cm}^{-1}/T)]^2. \quad (\text{A3})$$

This partition function reflects spin-orbit structure of the ^3P sulfur atom, with five degenerate lowest energy states of $J = 2$, three excited states of $J = 1$ and the upper non-degenerate $J = 0$

867 state. Experimental energy values were taken from the NIST database that, in turn, cites Martin
868 et al., 1990. With this input, for $^{32}\text{S}^{32}\text{S}$, we obtain $Q_{\text{tr}} = 61.79 \text{ \AA}^{-3}$ and $Q_{\text{el}} = 30.32$, at room
869 temperature $T = 298 \text{ K}$.

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Figure Captions

Fig. 1: a) Potential energy function of S_2 computed in this work. Black symbols indicate ab initio data, orange line is their cubic fit. Rotational potential for $j = 50$ state of S_2 (blue) is also shown for comparison;

b) Rotationally distorted potential of S_2 (green line), which includes the potential energy function (orange) and the centrifugal term (blue). Definitions of major terms are given for a typical scattering resonance trapped behind the barrier (shown by red dash). The asymptotic region ($S+S$) and the bound state region (S_2), are indicated for clarity.

c) Wave functions for two representative scattering resonances in S_2 (red lines). Resonance properties in each case are indicated for convenience. The energy range of scattering resonances (S_2^*) is indicated.

Fig. 2: Properties of individual scattering resonances in S_2 : a) Resonance width as a function of rotational quantum number j . Vibrational quantum numbers v are indicated. Rotational states with the same v but different j are connected by black line for convenience. b) Resonance width as a function of resonance energy relative to the top of centrifugal barrier. Dots to the right of dashed line (green) corresponds to broad over-the-barrier resonances. Dots to the left of the line correspond to narrow behind-the-barrier resonances.

Fig. 3: Resonance width computed using a simple analytic model, plotted vs. the value of width computed numerically by solving Schrodinger equation. Red dots correspond to individual resonances in S_2 . Good agreement through six orders of magnitude range of values is obtained. No fitting parameters are involved.

Fig. 4: Contributions of individual scattering resonances into the recombination rate coefficient, plotted as: a) a function of rotational excitation; b) a function of resonance width; c) a function of resonance energy with respect to the barrier top. The ranges of important values of j , Γ and δE can be easily identified. The total number of important resonances is on the order of one hundred (if both even and odd j values are included).

Fig. 5: Same as in Fig. 4 but calculated with the value of stabilization cross section scaled down individually for each resonance to reflect delocalization of its wave function. One can see that the value of rate constant is slightly reduced, and the important ranges of resonance properties are slightly shifted.

Fig. 6: Recombination rate coefficient as a function of mass of the second sulfur atom in S_2 , with first atom being ^{32}S . Viewed in a broad range of mass (upper frame) this dependence exhibits a “zigzag” behavior that looks nearly random. Focusing on a small range of mass (lower frame) helps to see that this behavior is explained by appearance of new vibrational states in the resonance spectrum. Several representative examples are annotated by rotational and vibrational quantum numbers. Between those events (on even smaller range of mass, indicated by green area in the lower frame) the dependence is monotonic, but very sharp. Red line gives linear fit of the data and shows the average trend that corresponds to classical mass-dependent behavior. Individual quantized resonances are responsible for mass-independent effect.

Fig. 7: Same as in Fig. 6a, but the vertical scale is different, and, in addition to the zigzag dependence (blue, computed using one constant value of stabilization cross section for all resonances) the results obtained by scaling down the value of stabilization cross section, individually for different resonances, are given (pink and green, using two somewhat different methods of scaling). Results of the analytic resonance-at-the-top model are also plotted for comparison (orange). All data indicate weak negative mass dependence.

Fig. 8: Contributions of different j values into the rate coefficient of recombination, computed using analytic resonance-at-the-top model for two isotopomers of S_2 . The source of negative mass dependence is clearly seen around $j = 50$.

Fig. 9: Schematic explanation of sudden (and thus mass-independent) increase of recombination rate coefficient due to appearance of new resonance near the top of the barrier, when the mass of sulfur atoms is raised. Green line shows the rotationally distorted potential energy curve, as in Fig. 1b-c. Top of the barrier is clearly seen. Left frame corresponds to lighter mass, and contains three resonant states trapped behind centrifugal barrier (red dashes). Right frame corresponds to heavier mass, and has the same three states, but now

1080 shifted to lower energies. This gives enough “space” to fit one more resonant state, just
1081 above the barrier top.

1082

Tables and Table Captions

1083

Table I. Characteristics of resonances in the analytic top-of-the-barrier model for two
1084 representative values of rotational excitation and for two extreme isotopomers of S₂ molecule.

Parameter	Isotopomers		% deviation*
$m_2 (amu)$	32	36	+12.5
$\mu (amu)$	15.986	16.926	+5.88
Calculations with $j = 50$			
$r^\ddagger (a_0)^{**}$	10.447	10.518	+0.68
$E^\ddagger (cm^{-1})$	64.958	60.107	-7.47
$\Gamma (cm^{-1})$	2.0771	2.0559	-1.02
$K_{eq} (a_0^3)$	0.7972	0.7490	-6.02
$\kappa (10^{-34} cm^6 / s)$	0.2422	0.2250	-7.10
Calculations with $j = 120$			
$r^\ddagger (a_0)$	7.800	7.872	-0.92
$E^\ddagger (cm^{-1})$	671.46	622.03	-7.36
$\Gamma (cm^{-1})$	6.6781	6.6138	-0.96
$K_{eq} (a_0^3)$	0.1018	0.1186	+16.52
$\kappa (10^{-34} cm^6 / s)$	0.0315	0.0362	+15.20

1085

* Relative to the major isotopomer

1086

** a_0 is Bohr radius, the atomic unit of length

Table II. Recombination rate constant κ_{ET} computed using constant stabilization cross section

Isotopomer	Reduced Mass	All j included		Only odd j included	
		Rate constant*	% deviation**	Rate constant*	% deviation**
$^{32}\text{S}^{32}\text{S}$	15.986035	2.4479	0.00%	<u>1.2183</u>	0.00%
$^{32}\text{S}^{33}\text{S}$	16.232038	<u>2.4502</u>	+0.09%	1.2653	+3.86%
$^{32}\text{S}^{34}\text{S}$	16.469883	<u>2.3840</u>	−2.61%	1.1940	−2.00%
$^{32}\text{S}^{36}\text{S}$	16.926058	<u>2.3499</u>	−4.00%	1.1654	−4.34%
$^{34}\text{S}^{34}\text{S}$	16.983935	2.3830	−2.65%	<u>1.1621</u>	−4.61%

* Units are $10^{-33} \text{ cm}^6/\text{s}$

** Relative to the major isotopomer

Table III. Recombination rate constant κ_{ET} computed using scaled stabilization cross section

Isotopomer	Reduced Mass	All j included		Only odd j included	
		Rate constant*	% deviation**	Rate constant*	% deviation**
$^{32}\text{S}^{32}\text{S}$	15.986035	0.7806	0.00%	<u>0.3903</u>	0.00%
$^{32}\text{S}^{33}\text{S}$	16.232038	<u>0.7743</u>	−0.81%	0.3894	−0.23%
$^{32}\text{S}^{34}\text{S}$	16.469883	<u>0.7674</u>	−1.69%	0.3825	−2.00%
$^{32}\text{S}^{36}\text{S}$	16.926058	<u>0.7546</u>	−3.33%	0.3783	−3.08%
$^{34}\text{S}^{34}\text{S}$	16.983935	0.7531	−3.52%	<u>0.3756</u>	−3.77%

* Units are $10^{-33} \text{ cm}^6/\text{s}$

** Relative to the major isotopomer

Table IV. Recombination rate constant κ_{ET} computed using analytic top-of-the-barrier model

Isotopomer	Reduced Mass	All j included		Only odd j included	
		Rate constant*	% deviation**	Rate constant*	% deviation**
$^{32}\text{S}^{32}\text{S}$	15.986035	1.7966	0.00%	<u>0.8972</u>	0.00%
$^{32}\text{S}^{33}\text{S}$	16.232038	<u>1.7784</u>	−1.01%	0.8882	−1.00%
$^{32}\text{S}^{34}\text{S}$	16.469883	<u>1.7612</u>	−1.97%	0.8796	−1.96%
$^{32}\text{S}^{36}\text{S}$	16.926058	<u>1.7290</u>	−3.76%	0.8635	−3.76%
$^{34}\text{S}^{34}\text{S}$	16.983935	1.7262	−3.92%	<u>0.8621</u>	−3.91%

* Units are $10^{-33} \text{ cm}^6/\text{s}$

** Relative to the major isotopomer