# Reaction of excited $S_2(a^1 \Delta_g)$ with $H_2 S$

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Abstract: Rate constant of reaction of lowest electronically excited state of  $S_2$  with  $H_2S$  was calculated from first principles. The potential energy surface for the reaction  $S_2(a^1\Delta_g) + H_2S \rightarrow SH + HS_2$  was calculated using state-of-the-art quantum chemistry methods. The results of modeling provide fundamental information on the interaction of hydrogen sulfide with the electronically exited  $S_2$ . The effective rate constant of the reaction was calculated within the framework of stochastic approach and transition state theory in the temperature range of T = 500 - 2000 K.

Keywords: H<sub>2</sub>S, excited S<sub>2</sub>, rate constant

#### 1.Introduction

Decomposition of H<sub>2</sub>S has been investigated for a long time [1]. Reaction  $S_2 + H_2 S \rightarrow SH + HS_2$  (R1) is a part of the chemical mechanism of the thermal decomposition of the hydrogen sulfide [2]. In the work [2] an estimation of the rate constant of the reaction was made based on the *ab*initio calculation and transition state theory (TST). It was shown that this reaction is endothermic (1.41 eV) and likely does not have a notable barrier. It is the reason for a very low rate constant 10<sup>-18</sup>-10<sup>-19</sup> cm<sup>3</sup>/s at low and moderate temperatures. Yet, thermal decomposition of H<sub>2</sub>S is accompanied by formation of atomic sulfur S(<sup>3</sup>P). The recombination of atomic sulfur at relatively low temperatures leads to formation of molecular sulfur  $(S_2)$  in electronically excited states. One of them is the long living metastable state - the lowest singlet state  $S_2(a^1\Delta_g)$  which only slowly decays to ground state  $S_2(X^3 \Sigma)$  because this process is formally spin-forbidden. A similar situation takes place in the case of non-equilibrium plasma, where S(<sup>1</sup>D) forms also together with  $S(^{3}P)$ .

Quite often, reactions with participation of molecules in excited state are faster than corresponding reactions with ground states because of "improvement" of reaction thermo-chemistry (e.g., the difference of formation enthalpy of  $S_2(a^1\Delta_g)$  and  $S_2(X^3\Sigma)$  is about 0.6 eV). However, real acceleration of the processes is determined not only by energy but also the presence or absence of the barriers along the reaction pathway:

$$S_2(a^1\Delta_q) + H_2S \iff SH + HS_2 \tag{R2}$$

To understand how excitation of molecular sulfur to the lowest excited state affects reaction characteristics it is necessary to investigate potential energy surface (PES) of the reaction and to determine parameters of the transition states (TS) along reaction pathway.

This work is devoted to analysis of the interaction of  $H_2S$  with the first metastable electronic state of sulfur  $S_2(a^1\Delta_g)$ .

#### 2.Methods

It is important to note that recombination of atomic sulfur occurs at relatively low temperatures. Equilibrium constant of reaction of molecular sulfur dissociation is 1 at  $\sim 3500$  K. It imposes strong restriction to accuracy of used methods for calculation of PES and rate constant. That is why the rate constant of the reaction (R2) was calculated as follows:

- calculation of PES of reaction and location of intermediate and transition states (TS) using state-of-the art *ab-initio* quantum chemistry (QC) methods
- calculation of reaction rate constant based on stochastic approach and transition state theory (TST).

#### 2.1 Calculation of PES of the reactions R1, R2

The fragment of PES for the reaction R2 were computed using Firefly QC package [3]. The zero-order wavefunctions were obtained from Complete Active Space Self Consistent Field (CASSCF) computations with active space formed by 16 electrons distributed over 12 active orbitals and then corrected using Extended Multi-Configuration Quasi-Degenerate Perturbation Theory at second order (XMCQDPT2) [4]. The averaging over four lowest singlet states (SA4) was applied. The correlationconsistent basis set of triple-zeta quality (cc-pVTZ) was used throughout. Fragments of PES of reaction in ground state (R1) were computed as well at DFT level of theory. Becke 3-term correlation and Lee, Yang, Parr exchange functional (ub3lyp) was used. The 6-311 basis set was supplemented by diffuse 3df and 2pd functions. Such choice provided accuracy of thermochemical data on the level 0.06 eV. Indeed, calculated enthalpy of reaction (R1) 32.4 kcal/mole is closed to data from other sources [2], [5] 33.1-32.4 kcal/mole. The latter was done to identify the parameters of transition state (not reported in the work [2]) and to recalculate reaction characteristics with higher accuracy.

Pathway of reactions (R1) and (R2) is shown on the Fig.1.The origin of the energy corresponds to reagents of reaction (R2). Reaction (R1) is barrier-less. The difference between TS3 and products  $HS+HS_2$  is in the range of accuracy of the chosen QC method. This result is in the agreement with conclusion of the work [2]. Accuracy of the calculated PES is confirmed by comparison with available thermochemical data for reagents and products [2], [5]:

 $\Delta H (S_2(a^1 \Delta_a) = 0.6 \, eV, \Delta H (HS+HS_2) = 0.84-0.87 \, eV$ 

The reaction (R2) proceeds via transition state TS1 with formation of global minimum  $H_2S_3^*$  at energy -0.47 eV. The first step of reaction has activation barrier of 0.33 eV. Direct formation of the products is difficult because of difference in the geometry of  $H_2S_3^*$  and HS and HS<sub>2</sub>. That is why formation of second intermediate state  $H_2S_3^{**}$  takes place. Indeed, the reaction proceeds by formation of second local weakly bound minimum  $H_2S_3^{**}$  through second transition state TS2. The difference of energies of these states is only 0.03 eV. This peculiarity is important for micro kinetic analysis because intermediate state is highly unstable in respect of the reverse process. Finally, decay of the weakly bound minimum leads to formation of the products of the reaction HS and HS<sub>2</sub>.



Fig. 1. Potential energy surface for the reactions R1, R2 along with geometries of transition states (TS1,2,3) and minima of reactions R2.

# 2.2 Rate constant calculation.

Analysis of reaction pathway of reaction (R2) shows that formation of weakly bound complex  $H_2S_3^{**}$  cannot effect upon value of overall reaction rate because of low stability of the complex. As it was mentioned before this complex decay quickly to  $H_2S_3^*$ . That is why overall process can be regarded like sequence of two reactions: first is formation of a stable intermediate complex  $H_2S_3^*$  with explicit rigid transition state TS1 and, second, is decay from the stable intermediate complex to products without explicit barrier (loose TS):

$$S_2(a^1\Delta_g) + H_2S \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} H_2S_3 * \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} SH + HS_2$$
(R2).

In the first process, the system passes through a potential barrier with a height of 0.329 eV where the transition state TS1 is localized. The dissociation of the intermediate complex into the product area is endothermic process with  $\Delta$  H<sub>TS1</sub>=1.34 eV. However, H<sub>2</sub>S<sub>3</sub>\*(v) is formed in vibrationally excited states, and reaction proceeds via chemically activated complex. This means that a real value of  $\Delta$ H<sub>TS1</sub> can be much lower and the rate of decay is determined by branching ratio of H<sub>2</sub>S<sub>3</sub>\* decay and collisional vibrational relaxation:

 $H_2S_3^*(v)+M \rightarrow H_2S_3^*(v-1)+M$ 

The overall rate constant of reaction (R2) was estimated from solution of time-dependent Master Equation for possible intermediate states using "MultiWell" package [6]. The stochastic approach was applied. In addition, the Canonical Transition State Theory (TST) was used to check obtained results in the cases of lack of deficient statistical data. Results of both approaches are shown on Fig.2. The geometries and vibrational frequencies of reagents, TSs and intermediate complexes were taken from QC calculations. For barrier-less reaction  $k_2$ , the position of virtual TS was determined using hindered rotation Gorin model [6].

Rate constant of the reaction (R1) was calculated in framework of TST theory using results from QC calculations. Obtained value are in good agreement with the results reported in [2].

# 3. Results and discussion.

Figure 2 shows the results of the above calculations of the rate constant (R2) in comparison with reaction in ground state (R1), calculated by TST by Sendt [2]. Participation of electronically excited state of S<sub>2</sub> leads to essential acceleration of the reaction. Let us note that due to complex character of PES (presence of stable intermediate complex, existence of barriers for complex decomposition to the reagents) obtaining constant for the excited state cannot be estimated by simple decrease in the activation energy by the value of the excitation energy  $\Delta H=$ - $\Delta H_f(S_2(a^1\Delta_g)) - \Delta H_f(S_2(X^3\Sigma)) = 0.6 \text{ eV}$ . As expected, rate constant of reaction (R2) is much higher than rate constant of the reaction (R1). For the characteristic temperature T =1000 K, the constants differ more than four orders of magnitude. Temperature increase leads to "convergence" of the rate constants due to input thermal energy in the process along with excitation energy. The Arrhenius approximation of reaction rate constants:

 $k_{R2}$ =1.1\*10<sup>-7</sup>(T/300)<sup>-2.2</sup>exp(-11800/T), cm<sup>3</sup>/s,  $k_{R1}$ =6.71\*10<sup>-12</sup>exp(-16628/T), cm<sup>3</sup>/s, where T -temperature in K.



Fig. 2. Rate constants. Reaction (R1) – blue line. Reaction
(R2) – TST calculation: red line, Master Equation solution: stars. Dashed area- estimation of calculation error.

#### 4.Conclusions

The rate constant of the reaction of hydrogen sulfide with electronically excited metastable sulfur was calculated from the first principles. Reaction has complex PES with stable intermediate states. These peculiarities along with participation of exited metastable  $S_2$  in the reaction lead to significant (several order of magnitude) increase of rate constant in comparison with reaction in ground state. This result may be important for analysis of  $H_2S$  decomposition in different type of the discharges where electronically excited  $S_2$  is formed.

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# **5.References**

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