

Thermal energy charge transfer between S^{2+} and H_2 , N_2 , and CO

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We measured the charge transfer rate coefficients for the reactions $S^{2+} + H_2 \rightarrow$ products, $S^{2+} + N_2 \rightarrow$ products, and $S^{2+} + CO \rightarrow$ products using a radio frequency trap. S^{2+} ions are produced by laser ablation of a solid tungsten disulfide target. We derive the rate coefficient of the reaction from the decay rate of the stored ions in the trap. The rate coefficients for the above three reactions are $1.58(0.13) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at $T_{\text{equiv}} = 1077 \text{ K}$, and $1.67(0.12) \times 10^{-9}$ and $1.78(0.13) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ at $T_{\text{equiv}} = 6462 \text{ K}$.

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INTRODUCTION

Sulfur is one of the abundant, heavier elements produced through stellar nuclear synthesis. The emission lines from various ionization stages of sulfur have been observed and used for plasma diagnostics in a wide range of astrophysical regions and in objects such as HI regions, molecular clouds, interstellar medium, quasars, x-ray photoionized nebulae, and planetary nebulae. These multiply charged ions of sulfur are formed by photoionization and they coexist with neutral helium and hydrogen as well as other molecules. Since these regions are not in thermodynamic equilibrium because of the low particle density [1], the distribution of the elements among the various ionization stages is governed by several competing processes. These processes include charge transfer recombination and ionization, dielectronic recombination, radiative recombination, and electron impact ionization. In a neutral rich environment, charge transfer recombination or ionization can be the dominant process that controls the states of ionization in astrophysical plasmas [2–6]. For example, charge transfer of solar wind heavy ions has recently been confirmed as a major excitation mechanism for x-ray sources in comets [7–9]. For a realistic modeling of astrophysical plasmas, it is of paramount importance that the charge transfer recombination and ionization rate coefficients of multiply charged ions such as sulfur be known accurately at the temperature of these environments.

Despite its importance, no experimental studies have been made on sulfur ions at eV energies. Moreover, quantal treatments of low-energy collisions are also unavailable. This may be due, in part, to the complicated electronic, vibrational, and rotational structures of the molecules and the availability and accuracy of the position and orientation sensitive potentials of the pseudomolecule formed during the collision. An experimental study of the charge transfer processes of S^{2+} with atoms and molecules is therefore particularly useful, not only to explain the ionization structures in astrophysical plasmas, but also to stimulate theoretical treatments in this energy range.

I. EXPERIMENTAL METHOD

The experiment was carried out using a technique that combines a laser ablation ion source and ion storage. A detailed discussion of the technique and the description of the

facility have been published earlier [10] and will not be repeated here. In the following, we shall highlight only the details as they pertain to this measurement. One of the unique features of this technique is its ability to produce and store a single type of ion to be studied without contamination of a carrier gas. The S^{2+} ions were produced directly by laser ablation of solid tungsten disulfide (WS_2) targets. We chose tungsten disulfide as the target material over pure sulfur and other solid compounds of sulfur, such as zinc sulfide (ZnS) and tantalum disulfide (TaS_2), because of the reproducibility of the ion signal in the trap. Furthermore, S^{2+} ($m/q=16$) and other low-charge-state ions such as S^+ ($m/q=32$), W^+ ($m/q=184$), W^{2+} ($m/q=92$), and W^{3+} ($m/q=61.3$) that were produced simultaneously during laser ablation have a distinct difference in their mass-to-charge ratios. These ions can be excluded from the ion trap by a judicious choice of the trapping parameters. In these measurements, we used approximately 10 mJ/pulse of the second harmonic (532 nm) output emission of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser as the ablation source. The power density of the laser at the ablation target surface was estimated to be about 10^9 W cm^{-2} . We limited the power of the laser to eliminate the formation of higher-charge-state ions of tungsten and sulfur.

The ion trap parameters were set at a rf of 1.00 MHz, ac amplitude $V_0=360 \text{ V}$, and dc bias $U_0=35 \text{ V}$ to store S^{2+} . The characteristics of the trap can be found in a previous publication [10]. The set parameters generated a pseudopotential well for S^{2+} with an axial well depth of $qD_z=17 \text{ eV}$ and a radial well depth of $qD_r=39 \text{ eV}$. At these trap parameters, the low-charge-state tungsten ions and the singly charged sulfur ions were in the unstable region of the trap and were not stored in the trap.

The stored ions in the trap were analyzed by extracting all of the ions from the trap by two push-pull voltage pulses (+200 V and -200 V) applied simultaneously at the end caps of the trap. The extracted ions were then injected into a time of flight (TOF) mass spectrometer. They were focused by an electrostatic lens in the TOF tube to a 1-in.-diameter microchannel plate detector assembly. The signal output of the multichannel plate is amplified by a $\times 40$ preamplifier before it is fed into the terminated input of a digital scope through a 50Ω impedance matched transmission line. The use of a transmission line enables us to preserve the temporal profile of the stored ions as they are intercepted by the de-

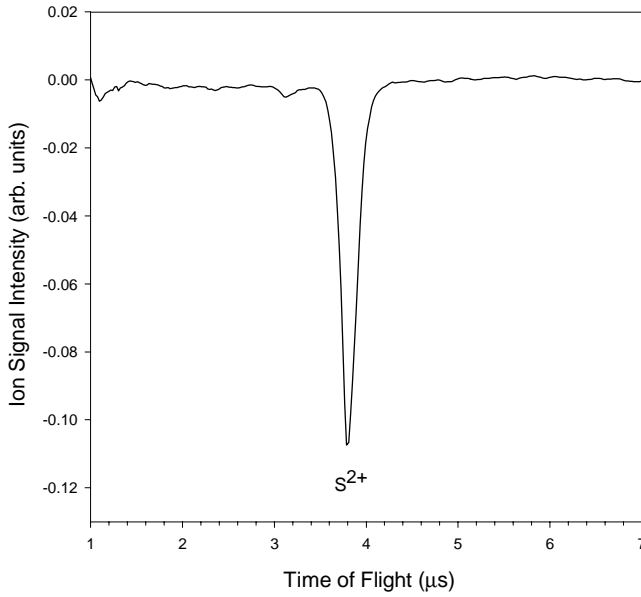
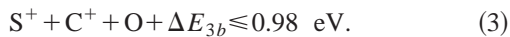
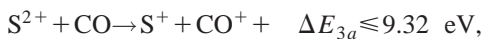
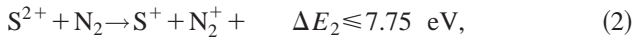


FIG. 1. Time of flight mass spectrum of the S^{2+} ions released from the trap after 0.4 s storage time.

tector. As part of an ongoing effort to improve the mass resolution, the length of the TOF drift tube in the ion trap-detector system has been increased from 0.3 to 0.58 m. The mass resolution ($m/\Delta m$) of the current system is about 18 at mass 16. While the time of flight of the ion signal was used to identify the type of ion, the integrated ion signal $I(t) = \int_{\Delta t} S(t) dt$ [where $S(t)$ is the time dependent ion signal recorded in the digital scope and Δt is the duration of the ion signal] was used to measure the relative S^{2+} population stored in the trap prior to their extraction. Figure 1 shows the TOF mass spectrum of the stored S^{2+} ions in the trap. The single peak indicates that only S^{2+} ions are stored in the trap. The $1/e$ decay time for the stored ions has been measured to be in excess of several minutes at the base pressure of 4×10^{-10} Torr.

The ground state of S^{2+} is 33.69 eV above its neutral ground state. The reaction channels with both single and double electron capture from reactant molecular gas are energetically possible, for example,



However, the parameters of the trap were set to store only S^{2+} . Ions with m/q greater than 18 or smaller than 8 are outside the stable region of the trap and will not be stored. Low-charge-state tungsten ions, S^+ ions formed during laser

ablation, and all product ions produced by single electron transfer and double electron transfer were also excluded from the trap. For this measurement, our present facility allows us to measure only the total charge transfer rate coefficient.

The mean relative integrated ion signal $I_r(t)$ is related to the total charge transfer rate coefficient k by a single exponential function:

$$I_r(t) = \exp[-R(t-t_0)], \quad (4)$$

with

$$I_r(t) = (1/N) \sum_{N=1}^N [I(t)/I(t_0)]_N \quad (5)$$

and

$$R = n_m \langle v_1 \sigma_1 \rangle + n_b \langle v_2 \sigma_2 \rangle = n_m k + R_b, \quad (6)$$

where N is the number of individual measurements, n_m is the density of the reactant gas, n_b is the density of the residual background gas in the ultrahigh-vacuum chamber, $I_r(t)$ is proportional to the number of S^{2+} ions at time t , and σ_1 and σ_2 are the charge transfer cross sections to all channels including single and multiple electron transfer with the reactant molecular gas and with residual gas, respectively. v_1 and v_2 are the relative velocities of the interacting multiply charged ions with reactant gas molecules and the residual gas molecules, respectively. R_b is the decay rate of S^{2+} ions in the ultrahigh-vacuum system with only residual background gas present. $I_r(t)$ is obtained by taking the ratio of the integrated ion signal at a delay time t , $I(t)$, and at the shortest delay time of 0.4 s, $I(t_0)$. This procedure minimizes the measurement error due to the short-term fluctuation and the long-term drift of the ion signal caused by the random change of the laser power and the gradual change of the surface conditions of the target as the ablation laser drills into the target. More than a hundred cycles for each delay time were carried out. We measured the integrated ion signal at about ten different storage times over one decade of the initial value at the shortest delay to obtain an ion decay curve.

The data set containing the mean relative integrated ion signal $I_r(t)$ was fitted to Eq. (4) using the weighted least-squares method. The weight for each point is determined from its statistical uncertainty. The decay rate R and its statistical uncertainty were determined from the fitting algorithm. The rate coefficient k was obtained by a weighted least-squares fit of the decay rates R at each reactant molecular gas density n_m to Eq. (6). The uncertainty of the rate coefficient was a quadratic sum of the statistical uncertainty derived from the data fitting and the uncertainty of the reactant gas density measurement. Absolute calibration of the ion gauge to measure the reactant gas density has been described in a previous publication [10] and will not be elaborated here.

The charge transfer rate coefficients were obtained from the slope of the decay rates of the stored ions in the presence of a reactant gas of known density. Since the ions are produced directly from a solid target, the complexities and un-

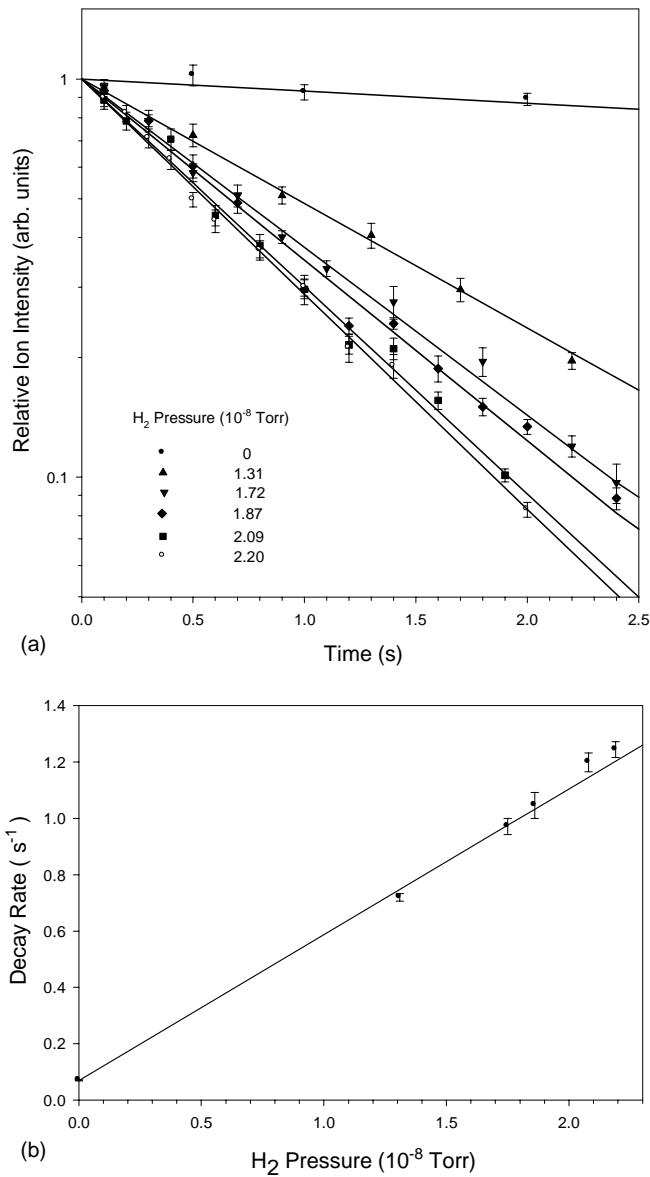


FIG. 2. (a) Decay curves of normalized relative intensity of S^{2+} ions vs storage time at six different pressures of H_2 in a pseudopotential well with $qD_z = 17$ eV and $qD_r = 39$ eV. The solid line is the least-squares fit to a single exponential function. (b) S^{2+} decay rate vs H_2 pressure.

certainties caused by the interaction between the ions and their carrier gas, as in some conventional ion source, are totally eliminated. In all the measurements, ultrahigh-purity grade or research grade reactant gases were used. The purity of the neutral reactant gas in the reaction chamber was further confirmed by a Vacuum Generator DX-100 quadrupole residual gas analyzer.

II. DATA ANALYSIS AND RESULTS

Figure 2(a) shows the time dependence of $I_r(t)$ at six different H_2 pressures. The solid lines represent the result of the weighted least-squares fit. Figure 2(b) plots the decay rates as a function of H_2 pressure. The slope of the solid line

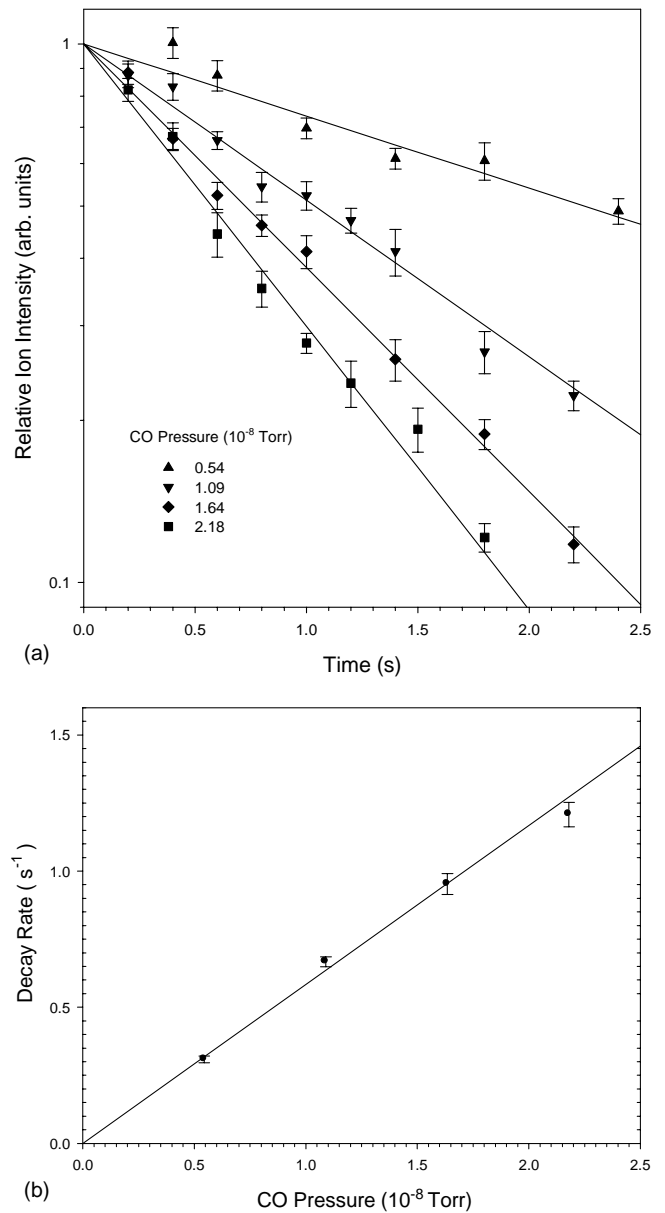


FIG. 3. (a) Decay curves of normalized relative intensity of S^{2+} ions vs storage time at four different pressures of CO. The solid line is the least-squares fit to a single exponential function. (b) S^{2+} decay rate vs CO pressure.

gives the charge transfer rate coefficient of $1.58(0.13) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. In a similar way, Figs. 3(a) and 3(b), 4(a) and 4(b) show the results of the reactions $S^{2+} + CO \rightarrow \text{products}$ and $S^{2+} + N_2 \rightarrow \text{products}$, respectively. The rate coefficient of S^{2+} with CO is $1.78(0.13) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ and of S^{2+} with N_2 is $1.67(0.12) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. The estimated uncertainty of the result is mainly due to the uncertainty in the statistical fluctuation of the ion signal, $\pm 2.5\%$, and the uncertainty in the absolute calibration of the target gas densities, $\pm 8\%$.

III. DISCUSSION

The S^{2+} ions produced by laser ablation can be in a variety of excited states immediately after production. They

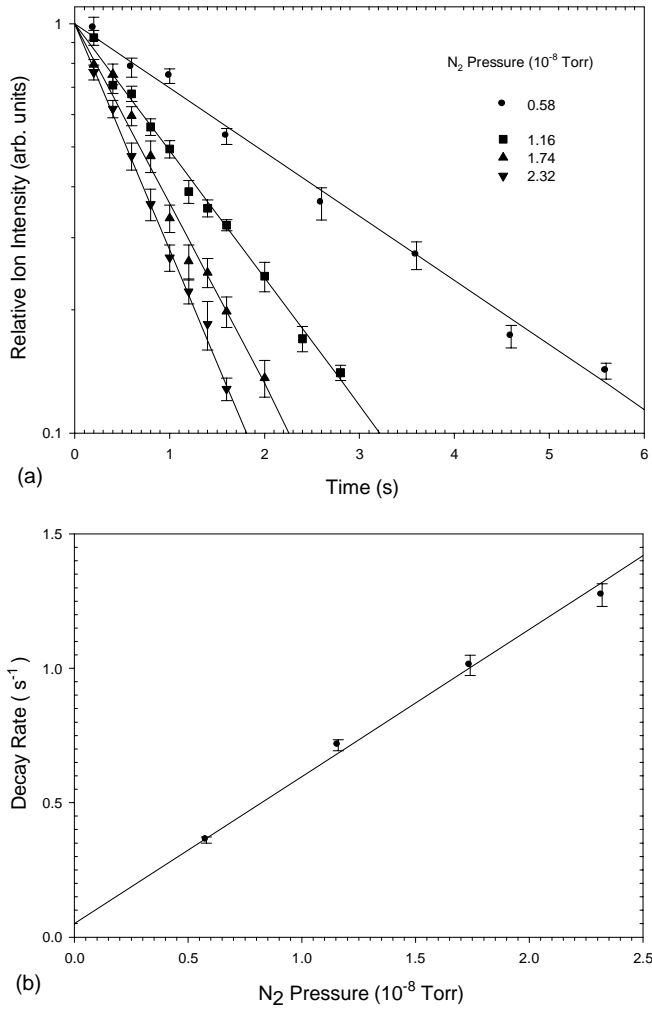


FIG. 4. (a) Decay curves of normalized relative intensity of S^{2+} ions vs storage time at four different pressures of N_2 . The solid line is the least-squares fit to a single exponential function. (b) S^{2+} decay rate vs N_2 pressure.

rapidly cascade to their ground state and low-lying metastable states through allowed transitions and collisional de-excitations by plasma electrons. We have shown in previous measurements that the ions stored in the trap produced by low laser power are in their ground state [11–13]. S^{2+} ions, however, unlike other ions we measured previously, have a $3p^2\ ^1D_1$ metastable state only 1.4 eV above the ground $3p^2\ ^3P$ term. This small energy gap can favor the population of the metastable state and, therefore, it is quite possible that a significant amount of S^{2+} ions can be in this low-lying $3p^2\ ^1D_1$ state. This can make the current result difficult to interpret.

The ratio of the number of $3p^2\ ^1D_1$ metastable state ions to that of $3p^2\ ^3P_J$ ground state ions depends on the density and the temperature of the plasma electrons during the self-similar expansion of the laser induced plasma in vacuum. The expansion dynamics of a laser induced plasma has been investigated by Dawson [14], Rumsby and Paul [15], Measures, Drewell, and Kwong [16], Drewell [17], and Kwong and Fang [11]. During the early phase of its expansion, the

plasma is highly collisional, and collision equilibrium is established between the light plasma electrons and the heavy neutral and charged species in the plasma. The internal temperature of the atomic and ionic species is closely coupled to the temperature of the plasma electrons through rapid collision. As the temperature of the plasma electron drops when its initial energy is converted to its directed energy of expansion, the internal temperature of the atomic and ionic species decreases rapidly. Since the time dependence of the electron density n_e is proportional to t^{-3} while the time dependence of the electron temperature T_e is proportional to t^{-1} [15], the internal temperature of the atomic and ionic species freezes out when n_e drops below the threshold density to maintain collisional equilibrium. In the case of the laser induced chromium plasma, the freeze-out population ratio between the $a\ ^5S_2$ metastable state and the $a\ ^7S_3$ ground state of neutral chromium was measured by Drewell [17] using simultaneous laser selective excitation of the metastable and ground state Cr atoms seeded in the chromium plasma. His finding reveals that the freeze-out population ratio between the metastable and ground states is about 10^{-3} . Since the power density of the ablation laser used in Drewell's measurement is similar to that in the current measurement, and the $a\ ^5S_2$ metastable state of Cr is only 0.94 eV above its $a\ ^7S_3$ ground state, it is reasonable to assume that the metastable fraction for laser produced S^{2+} ions is below 10^{-3} . If we assume that the rate coefficient for the metastable state ion is unreasonably large, i.e., five times larger than that for the ground state ion, the error introduced in the measurement is $\leq 0.5\%$, far less than the $\pm 9\%$ uncertainty of the measurement. We therefore conclude that the effect due to the metastable state ions is negligible.

The ground state $3p^2\ ^3P$ term has three fine structure levels. These fine structure levels are about 0.4 and 0.6 eV apart. If we assume a similar freeze-out collisional temperature as estimated by Drewell for a chromium plasma [17], all fine structure levels will be populated. Our measurements, therefore, reveal the charge transfer between H_2 , N_2 , and CO and the $3p^2\ ^3P$ ground term of S^{2+} ions with an unknown population of its fine structure levels.

The presence of H_2 , N_2 , and CO in the trap can affect the storage time of the ion in the trap through elastic collisions with the stored ions. However, the probability of S^{2+} in a potential well of 17 eV being kicked out of the trap by elastic collisions with reactant gas at room temperature (0.04 eV) is negligibly small. This loss mechanism can be ignored in the analysis.

The concept of ion temperature in a rf trap has been investigated extensively by several investigators in the past [18,19]. The existence of an ion temperature is essential in the correct interpretation of the rate coefficient $k = \langle v\sigma \rangle$, with v having a Maxwellian distribution and a charge transfer cross section σ that depends on the velocity. An experiment was carried by Knight and Prior [19] with a tunable laser to map out the ion distribution in a rf trap. The observed Gaussian distribution of stored ions in the trap implies a Maxwellian velocity distribution. This is consistent with the concept that ions stored in a rf trap have a temperature [19]. Based on these findings, the mean energy of the stored

S^{2+} ions is about 1.7 eV. This mean energy corresponds to an ion temperature of about 10^4 K, which can be calculated by using the relation between the mean energy E and the temperature $E = (3/2)kT$ since the velocity distribution of the ions in a rf trap is nearly thermal [19].

Because the temperature of the neutral reactant gas is at room temperature (300 K), we introduce an equivalent temperature that corresponds to the mean relative velocity of the S^{2+} and the reactant gas molecules [20]. This equivalent temperature T_{equiv} of the collisional system is given by

$$T_{\text{equiv}}/\mu = T_i/m_i + T_n/m_n,$$

where the ion temperature is T_i and the reactant gas temperature is T_n . m_i and m_n are the masses of the ions and the neutral species, respectively, and μ is their reduced mass.

Using this relation, the equivalent temperatures for each measurement are estimated to be 1077 K for S^{2+} with H_2 and 6462 K for S^{2+} with CO and N_2 . Our result for S^{2+} with H_2 is about 40% smaller than the multichannel Landau-Zener calculation ($2.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) using the H_2 ionization Franck-Condon factor [21]. A quantal calculation is not available in this energy region. To the best of our knowledge, no calculation, Landau-Zener or quantal, is available for comparison with the results for the reaction of S^{2+} with CO and N_2 .

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