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EMISSION SPECTRUM OF HYDROGEN SULFIDE IN A HELIUM AFTERGLOW

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Emission spectrum of H_2S from the interaction of $He(2^3S)$ with H_2S was observed in a fast flow system. Radiation from the excited fragments, $SH^+(A^3\Pi-X^3\Sigma^-)$ and H(Balmer series), was identified in the 300 - 500 nm region. It was presumed that the excited fragments arose from superexcited states of H_2S.

Spectroscopic analysis of the radiation resulting from collisions of rare-gas metastable atoms with molecules provides direct information about the energy states of the reaction products. A steady-state flowing-afterglow is an available technique in this field. Although the emission spectra of sulfur compounds in a helium afterglow have been investigated on OCS[1)] and CS_2,[2)] no studies have been carried out on H_2S. This communication describes the excitation of H_2S by collisions of helium 2^3S metastables.

The flowing-afterglow apparatus, which is basically the same as those of the previous investigators,[3,4)] is shown in Fig. 1. The reaction chamber was continuously evacuated by a 7000 ℓ/min rotary pump. Metastable atoms were produced in a 2450 MHz microwave discharge (60 - 80 W). After removal of charged particles, they were mixed with the reactant gas at about 14 cm downstream of the discharge section. The pressures of helium and the reactant gas were measured by a McLeod gauge to be 0.9 - 2 Torr and 0.01 Torr, respectively. The flow velocity at 1 Torr was estimated to be 4×10^4 cm/sec. Upon addition of H_2S gas, a blue conical flame appeared. The spectrum in the 300 - 500 nm region was observed through a quartz window with a Shimadzu GE-100 monochromator equipped with a 1200 lines/mm grating blazed at 500 nm, and an RCA 1P28 photomultiplier.

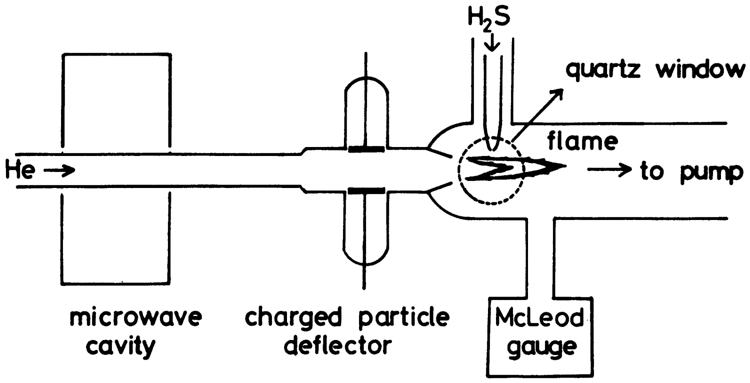

Fig. 1. The helium afterglow apparatus.

Figure 2 shows a typical emission spectrum in the 330 - 415 nm region. No appreciable change in the spectrum was found, when a dc voltage of 0 - 100 V was applied to the deflector. The observed spectrum is similar to the electron-impact spectrum at 200 eV.5) The most prominent band at 330 - 347 nm region is assigned to the (0,0) band of the $A^3\Pi$-$X^3\Sigma^-$ system of SH^+.6) The band in the 357 - 373 nm region, the structure of which is similar to the (0,0) band, is assigned to the (0,1) band of this system.7) The following atomic lines are also identified, although the HeI lines are observed as background spectrum: H(δ-4102 Å, ε-3970 Å) and HeI($3p^3P$-$2s^3S$ 3889 Å, $5d^3D$-$2p^3P$ 4026 Å). With a more sensitive measurement, new additional weak features were found in the 390 - 410 nm region, where the atomic lines of H_ε and HeI are overlapped. This band could be attributed to the (0,2) band of SH^+(A-X).

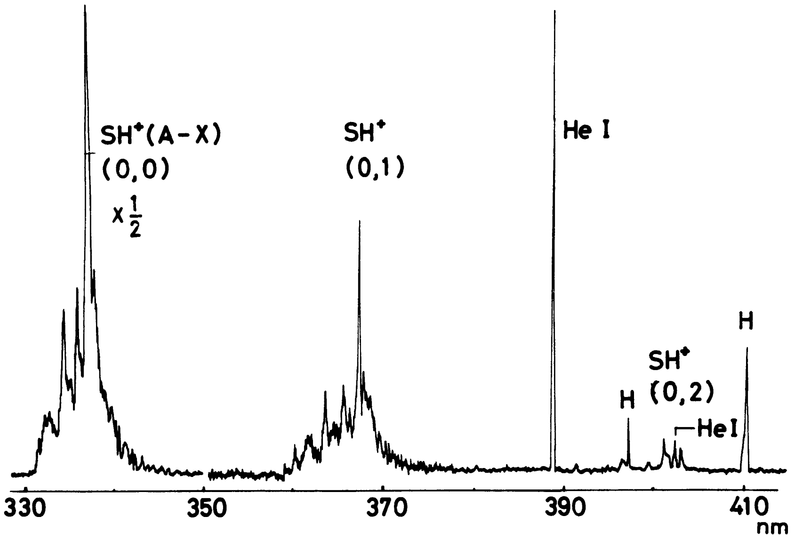

Fig. 2. Emission spectrum from the He(2^3S) + H_2S reaction. The pressures of He and H_2S were 1.6 and 0.01 Torr, respectively.

The spectrum in the 415 - 500 nm region consists of strong Balmer lines of the hydrogen atom, a few unassigned transitions, and several helium atomic lines (background).

However, any photoemission of $H_2S^+(A\text{-}X)$, which was observed under the electron-impact excitation,[5,8] could not be detected in the present study.

Since the contribution of charged particles to the observed emission is negligible under the present experimental conditions, the dominant exciting species is helium 2^3S metastable with an energy of 19.8 eV. Figure 3 shows the energy-level diagram for H_2S^+ observed by photoelectron spectroscopy[9] and the calculated dissociation limits leading to $H(n=4\text{-}7)$ and $SH^+(A)$. For the calculation, the following dissociation and ionization energies were used: D(HS-H)=4.3 eV[10] and I(SH)=10.4 eV.[11] It is clear from Fig. 3 that the responsible pathways for the formation of the excited hydrogen atoms are

$$He^*(2^3S) + H_2S \longrightarrow H(n=4\text{-}7) + SH(X^2\Pi) + He(1^1S).$$

The dissociation limits are above the first adiabatic ionization potential, and the remaining fragment is a neutral species. Therefore, the excited hydrogen atoms can only be formed through highly excited neutral states (superexcited states) of H_2S. The importance of the superexcited states in the excitation by rare-gas metastable atoms has been pointed out by Platzman[12] and Jesse.[13] They have shown that a significant fraction of molecular ionization takes place through superexcited states, from which dissociation into neutral fragments occurs competitively.

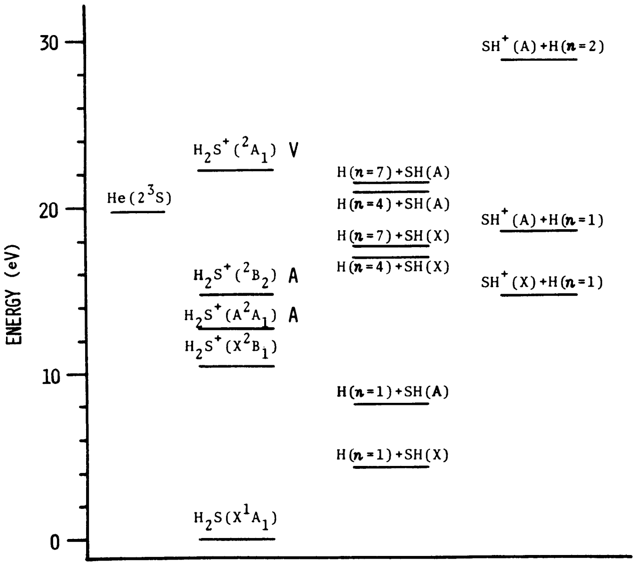

Fig. 3. Energy-level diagram of H_2S^+ and the dissociation limits leading to H and SH^+. A and V denote adiabatic and vertical IP, and no letter indicates A≃V.

Another important excited species produced in the $He(2^3S) + H_2S$ system is $SH^+(A)$, and the following reaction pathway is only energetically possible.

$$He^*(2^3S) + H_2S \longrightarrow SH^+(A^3\Pi) + H(n=1) + He(1^1S).$$

In this pathway, $SH^+(A)$ must be formed from some excited states of H_2S^+. According to the concept of Platzman and Jesse, H_2S^{+*} precursor states are mainly formed through some superexcited states. Since the dissociation limit leading to $SH^+(A)$ is located in a similar energy range to those leading to $H(n=4-7)$, $SH^+(A)$ is probably formed competitively through the same superexcited states. In recent investigations,$^{14)}$ most superexcited states have been interpreted in terms of high vibrationally excited Rydberg states converging to a certain ionic state. Similar Rydberg states of H_2S, which have not been observed, may exist in the 17.1 - 19.8 eV region and correspond to the superexcited states leading to excited H and SH^+.

In the present study, although intense photoemission from the excited fragments was observed, photoemission from the excited parent ion was absent. It can be concluded that favorite reaction pathways in the $He(2^3S) + H_2S$ system are the formation of the dissociation products through superexcited states and that the Penning ionization into $H_2S^+(A)$ is inefficient.

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