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Short Communication

Lifetime measurements on excited SH ($A^2\Sigma^+$) radicals

K. H. BECKER and D. HAAKS
Institut für Physikalische Chemie der Universität Bonn, Bonn (Germany)
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The H_2O and, very recently, the H_2S molecules have become of considerable interest for the chemistry of the interstellar medium. Both molecules have been detected by radio astronomy in interstellar clouds[1,2].

The H_2S photochemistry, contrary to that of H_2O, has not been studied very well. It is known that the vacuum-u.v. photolysis of H_2S, in a manner similar to H_2O photolysis, partly leads to the formation of electronically excited $SH(A^2\Sigma^+)$ radicals (Dyne and Style[3]). The dynamics and the quantum yield of the H_2S decomposition is different from that of H_2O, as was found recently (Haaks[4], and Becker and Haaks[5]).

The photodissociation of H_2S into excited $SH(A^2\Sigma^+)$ radicals and H atoms by irradiation with rare gas resonance lines at 1470 or 1236 Å can be used to measure the natural and collisional lifetime of $SH(A^2\Sigma^+)$. Such measurements were carried out by using mechanically modulated light pulses of a xenon or krypton resonance lamp for the pulse-photolysis of H_2S. The fluorescence decay after the excitation pulse was recorded by a cooled photomultiplier through an interference filter ($\lambda_0 = 3280$ Å, $\Delta\lambda = 100$ Å) with photon-counting techniques (Becker *et al.*[6]). The multiplier pulses were stored in a signal analyzer over a large number of scans.

The fluorescence decay measurements were made under flow as well as under static conditions. Figure 1 shows the inverse decay times of the exponentially decaying fluorescence as a function of the H_2S and D_2S pressure, respectively.

The fluorescence intensity follows the following reactions:

Excitation process:

$$H_2S + h\nu_{1236\ \text{Å}} \rightarrow SH(A^2\Sigma^+, v = 0) + H$$

Fluorescence decay:

$$SH(A^2\Sigma^+, v = 0) \rightarrow SH(X^2\Pi, v = 0) + h\nu_{3240\ \text{Å}};\ k_S$$

$$SH(A^2\Sigma^+, v = 0) + M \rightarrow SH(X^2\Pi, v = 0) + M;\ k_M$$

or products

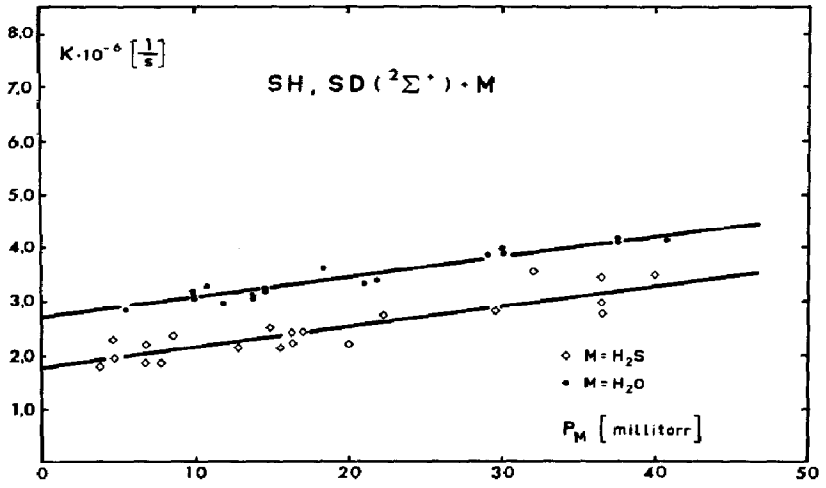

Fig. 1. The inverse of the fluorescence lifetime as function of the H_2S and D_2S pressure, respectively.

TABLE 1

NATURAL LIFETIMES AND OSCILLATOR STRENGTHS

$SH(A^2\Sigma^+, v = 0)$	τ_S : $(0.55 \pm 0.14) \times 10^{-6}$ s
$SD(A^2\Sigma^+, v = 0)$	τ_S : $(0.37 \pm 0.07) \times 10^{-6}$ s
$SH(A^2\Sigma^+, v = 0 \leftrightarrow X^2\Pi, v = 0)$	f_{00} : $(1.45 \pm 0.4) \times 10^{-3}$
$SD(A^2\Sigma^+, v = 0 \leftrightarrow X^2\Pi, v = 0)$	f_{00} : $(2.2 \pm 0.4) \times 10^{-3}$

Accordingly, the inverse lifetime of the emitting state is given by $1/\tau = k_S + k_M(M)$. From the extrapolation to the pressure (M) = 0 in Fig. 1 the natural lifetime $\tau_S = 1/k_S$ was derived. The natural lifetimes τ_S and the corresponding oscillator strengths f_{00} are given in Table 1.

In Table 2 the rate constants k_M as well as the cross sections of electronic quenching of the excited SH and SD radicals by different gases M are listed.

TABLE 2

QUENCHING CROSS SECTIONS, $T = 298$ K

M	$SH(A^2\Sigma^+, v = 0)$		$SD(A^2\Sigma^+, v = 0)$	
	k (cm³ molecule^{-1} s^{-1})	(Å)²	k (cm³ molecule^{-1} s^{-1})	(Å)²
H_2S	$(12.1 \pm 3) \cdot 10^{-10}$	196 ± 60		
D_2S	—	—	$(11.4 \pm 1.8) \cdot 10^{-10}$	187 ± 30
H_2*	$2.2 \cdot 10^{-12}$	0.12	—	—
N_2*	$4.5 \cdot 10^{-12}$	0.13	—	—
He*	$1.0 \cdot 10^{-12}$	0.075	—	—
Ar*	$6.0 \cdot 10^{-12}$	0.10	—	—
Ne*	$8.0 \cdot 10^{-12}$	0.11	—	—

* From Stern–Volmer plots with $\tau_S = 5.5 \times 10^{-7}$ s.

The natural lifetime τ_s and the f_{00} value may exhibit a slight dependence on the rotational energy as for $OH(A^2\Sigma^+)$, (Haaks[4] and Becker and Haaks[5]) which is under further investigation.

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