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Ubachs, W.M.G.; Termeulen, J.J.

published in

Journal of Chemical Physics
1990

DOI (link to publisher)

[10.1063/1.458000](https://doi.org/10.1063/1.458000)

document version

Publisher's PDF, also known as Version of record

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citation for published version (APA)

Ubachs, W. M. G., & Termeulen, J. J. (1990). LIFETIME OF THE A-2-SIGMA+, V'=0-STATE OF HS - COMMENT. *Journal of Chemical Physics*, 92(3), 2121-2122. <https://doi.org/10.1063/1.458000>

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Comment on: "Lifetime of the $A^2\Sigma^+, v'=0$ state of HS"

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(Received 21 May 1989; accepted 16 October 1989)

In a recent contribution to this Journal Loge and Tiee¹ report a new value for the natural lifetime of the $A^2\Sigma^+, v'=0$ state of the sulphur hydride radical. Using the Hanle effect they find a value of $\tau = 0.17\text{--}0.3$ ns. Previously Tiee *et al.*² had estimated the lifetime $\tau = 0.5\text{--}2$ ns from extrapolated quenching ratios. Friedl *et al.*³ found $\tau = 3 \pm 2$ ns by measuring time resolved fluorescence; they also experimentally determined the radiative lifetime of the $A^2\Sigma^+, v'=0$ state, $\tau_{\text{rad}} = 820 \pm 240$ ns, which is in good agreement with the value $\tau_{\text{rad}} = 704$ ns obtained in an *ab initio* calculation by Senekowitsch *et al.*⁴ A distinction is made between a natural lifetime τ , a predissociation lifetime τ_{pre} , and a radiative lifetime τ_{rad} related to the oscillator strength of the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition. The natural lifetime τ that obeys the relation

$$1/\tau = 1/\tau_{\text{rad}} + 1/\tau_{\text{pre}} \quad (1)$$

governs fluorescence decay, lifetime broadening and any other observable effects involving the excited state. For SH ($A^2\Sigma^+$) the predissociation clearly determines the natural lifetime. Less than 1% of the excited SH molecules will contribute to the fluorescence signals in a laser induced fluorescence (LIF) experiment.

Some years ago we published an accurate value for the lifetime of the $A^2\Sigma^+, v'=0, N=0$ state of SH: $\tau = 3.2 \pm 0.3$ ns.⁵ Moreover a strong dependence of the lifetime on the rotational quantum number N was observed. These results were obtained directly from spectral line broadening in a high resolution molecular beam experiment, using a continuous wave low power (1 mW) laser with a sub-MHz bandwidth. The conditions of a molecular beam allow for an essentially collision-free LIF detection environment. In the same molecular beam setup, with equal density in the molecular beam and background pressure ($< 5 \times 10^{-6}$ Torr) spectral lines of OD⁶ were measured with a linewidth of 1.5 MHz, thus ruling out any pressure effects in the linewidth measurements on SH.

The same method was used to measure the lifetime of the $C^2\Sigma^+, v=0$ state of CH,⁷ and in a refined version the lifetime of SiCl.⁶ For each single resolved hyperfine component in the $A^2\Sigma^+ \rightarrow X^2\Pi$ (0,0) rotational transitions of SH the broadening effect due to the fast predissociation was determined. The observed linewidths (fwhm) varied from 95 MHz for the low N states to 200 MHz for $N=9$. The treatment of subtracting the residual Doppler width in the molecular beam was discussed before.⁵ As we previously only presented the lifetime-broadening effects $\Delta\nu_\tau$, and in order to avoid confusion, we now wish to present the lifetimes of the $A^2\Sigma^+, v=0$ N states in Fig. 1. The values for the lifetimes

were derived using the equation:

$$\tau = 1/(2\pi \Delta\nu_\tau). \quad (2)$$

Figure 2 shows a recording of resolved hyperfine splittings in the $^2P_{21}(3)$ transition. The observed width $\Delta\nu \sim 100$ MHz sets a lower limit of $\tau > 1.6$ ns even if the residual Doppler contribution to the linewidth is ignored. A detailed study of the reduction of the Doppler width at different molecular beam divergences yields reliable values for the lifetimes of the rotational states with a 10% error margin. In a setup with minimized molecular beam divergence (Doppler width ~ 18 MHz) the $P_1(1)$ transition was measured with a total width of 54 MHz. From our spectra lifetimes of ~ 3 ns can be determined in a straightforward manner for the low N states. This is in clear contradiction to the findings of Loge and Tiee,¹ that were obtained by the rather indirect method of the Hanle effect. Our value is in excellent agreement with the findings of Friedl *et al.*,³ who reported a lifetime $\tau = 3 \pm 2$ ns. The statistical error in the latter value was too large to reveal the rotational effect upon the lifetime as discussed in this comment.

Figure 1 shows a tendency for the F_1 upper spin-doublet levels to have a shorter lifetime than the F_2 lower spin-doublet

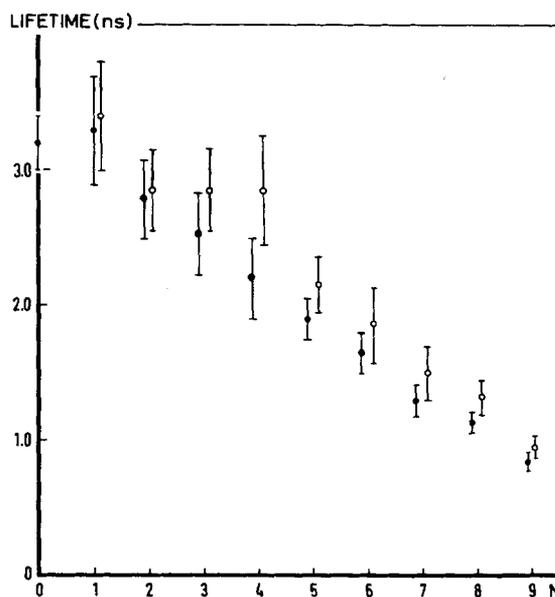


FIG. 1. Lifetimes of the $A^2\Sigma^+, v=0$ N states in SH; the black circles refer to F_1 states (upper spin-doublet), the open circles to F_2 states (lower spin-doublet).

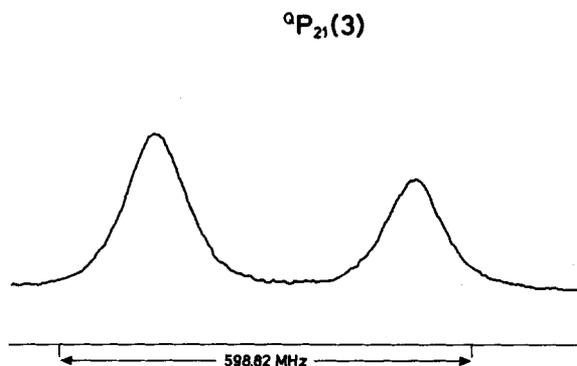


FIG. 2. Observed LIF spectrum of the $A^2\Sigma^+ - X^2\Pi$, $Q_{P_{21}}(3)$ and $Q_1(N)$ transitions in SH.

let levels. In a more recent reanalysis of the intensities in the observed spectra we found further evidence for a spin-doublet dependence of the predissociation lifetime. The ratio of observed intensities $Q_1(N)/Q_{P_{21}}(N)$ appears systematically lower than the ratio of the calculated rotational factors, based on transition matrix elements (Hönl-London factors) and laser-polarization effects.

The rotational state dependence of the predissociation rate has a large impact in all studies where LIF in the $A^2\Sigma^+ - X^2\Pi$ system is used as a probe for the determination of the $X^2\Pi$, rotational state population distribution. The SH product analysis in the photodissociation of H_2S (Refs. 8,9) will yield a rotational temperature that is systematically too low if the effects described above are ignored.

The authors wish to express their gratitude to Dr. Gerard Meijer for his cooperation and stimulating interest in this work.

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Reply to the Comment on: "Lifetime of the $A^2\Sigma^+$, $v'=0$ state of HS"

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(Received 11 April 1989; accepted 16 October 1989)

The contradiction between the two measurements of the lifetime, one using the Hanle effect¹ and the other measuring linewidths in a molecular beam,² can be explained as due to one of several possible effects. One possible explanation is a very fast collisional depopulation of the upper state (i.e., pressure broadening of the transition) in our gas phase measurement, which would not be present in the molecular beam experiment. This would require a gas kinetic collisional cross section approximately 1000 times larger than hard sphere to explain the observed lifetimes at 200 mTorr, which does not seem very likely although such large cross sections do occur. However, a more plausible explanation for the contradiction in measured lifetime is power broadening due to saturation of the $X^2\Pi_{3/2} \rightarrow A^2\Sigma^+$ transition using a

pulsed laser. For a peak intensity of 150 kW/cm^2 (estimated for a dye laser spot size of 2 mm diameter and $50 \mu\text{J/pulse}$) and a laser bandwidth of 0.08 cm^{-1} , a power broadened lifetime of 0.17 ns is predicted using the reported radiative lifetime of 700 ns obtained from an *ab initio* calculation.³ This is in good agreement with the reported lifetime of 0.17–0.3 ns using the pulsed dye laser.

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