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# Predissociation dynamics of the A $^{2}\Sigma^{+}$ state of SH and SD

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The technique of cavity ring-down spectroscopy has been used to investigate predissociation in the  $A^{2}\Sigma^{+}$  state of the SH and SD radicals. Spectra were recorded of the A-X (1,0) band of SH and the (1,0), (2,0) bands of SD. Linewidth measurements of transitions to individual rovibrational levels of the A state revealed increasing predissociation rates with vibrational and rotational quantum number. These and all other available data have been reproduced, quantitatively, by Fermi Golden Rule calculations employing the best (experimentally determined) analytic potential for the A state and *ab initio* repulsive potentials and spin–orbit coupling matrix elements. © 1997 American Institute of Physics. [S0021-9606(97)00543-6]

## I. INTRODUCTION

The SH radical is of importance in fossil fuel combustion processes and as an intermediate in a wide variety of naturally occurring reactions yielding sulphur containing pollutants. It is a direct product of  $H_2S$  photolysis in the upper atmosphere, and is of astrophysical relevance given the significant abundance of sulphur in the interstellar medium.

The SH A  ${}^{2}\Sigma^{+}-X$   ${}^{2}\Pi$  electronic transition was first observed in absorption by Lewis and White,<sup>1</sup> and has been the subject of numerous subsequent studies.<sup>2-7</sup> Ramsay,<sup>8</sup> and later Johns and Ramsay<sup>9</sup> used flash photolysis of H<sub>2</sub>S and  $D_2S$  to obtain UV spectra of the (0,0), (1,0), and (2,0) bands of the A  ${}^{2}\Sigma^{+}-X$   ${}^{2}\Pi$  transition of SH and SD using a grating spectrograph and performed a detailed rotational analysis. These workers reported sharp rotational lines in the (0,0)band while the (1,0) and (2,0) bands of SH were observed to be diffuse, indicating the onset of rapid predissociation. Ramsay<sup>8</sup> estimated rotational linewidths in the (1,0) band of  $\sim 0.1 \text{ cm}^{-1}$  implying a lifetime of SH A  $^{2}\Sigma^{+}$ , v'=1 of  $\sim$  50 ps. In comparison, the radiative lifetime of SH A  $^{2}\Sigma^{+}$ v' = 0 was experimentally deduced to be  $820 \pm 240$  ns (730)  $\pm 180$  ns for SD)<sup>10</sup> in fairly close agreement with *ab initio* calculations giving an estimate of 704 ns.<sup>11</sup> Further evidence for the predissociation of the A  ${}^{2}\Sigma^{+}$  state came from flame emission spectra<sup>12</sup> which showed the SH A-X (0,0) band and the SD A-X (0,0) and (0,1) bands, but no emission for v' > 0. Similarly, laser induced fluorescence (LIF) studies of SH and SD failed to detect fluorescence from v' > 0 levels of the A  ${}^{2}\Sigma^{+}$  state.<sup>13,14</sup> Excitation of SH on the A – X transition has been used to study SH-Ar and SH-Ar2 van der Waals complexes<sup>15</sup> and SH embedded in matrices of argon and krypton.<sup>16</sup> The presence of one or more Ar atoms bound to SH A  ${}^{2}\Sigma^{+}$  increased the fluorescence lifetime of v'=0 levels to as long as 600 ns; for Ar-SH the increase in the natural lifetime depended on the number of quanta of excitation of the Ar-SH stretch. SH contained within a rare-gas matrix showed complete quenching of the electronic predissociation of the *A*-state. More recently the SH A-X transition has been employed as a probe to measure nascent rotational distributions arising from the 266 nm photolysis of H<sub>2</sub>S using the technique of degenerate four-wave mixing (DFWM)<sup>17</sup> which, unlike LIF as a detection scheme, should not suffer from signal loss due to nonradiative processes such as predissociation.

Predissociation rates for SH and SD A  $^{2}\Sigma^{+}v'=0$  were determined accurately by LIF studies. Ubachs et al.<sup>18,19</sup> recorded high resolution LIF spectra of SH in a molecular beam to measure lifetime broadening of spectral lines and observed an N' dependence to the A  ${}^{2}\Sigma^{+}$  v'=0 predissociation rates. The natural lifetimes decrease monotonically from  $3.2 \pm 0.3$  ns for N' = 0 to  $0.95 \pm 0.02$  ns for N' = 9, with *e*-parity levels (corresponding to the  $F_1$  components of the  $A^{2}\Sigma^{+}$  state) having slightly shorter lifetimes than the f-parity ( $F_2$ ) levels. These lifetime values are in good agreement with the results of quenching<sup>20</sup> and time-resolved fluorescence decay experiments.<sup>10</sup> Kawasaki et al.<sup>21</sup> measured fluorescence lifetimes of SD A  $^{2}\Sigma^{+}$ , v'=0, N'=0-13 and observed a monotonic decrease with increasing N' from  $198\pm7$  to  $44\pm1$  ns, with *e*-parity levels again having slightly shorter lifetimes.

Electronic structure calculations<sup>22-24</sup> suggest that the interactions resulting in predissociation of the A  $^{2}\Sigma^{+}$  states of SH and SD are similar to those occurring in the OH radical. Predissociation of the OH A  ${}^{2}\Sigma^{+}$  state has been much studied both experimentally $^{25,26}$  and theoretically. $^{27,28}$  The  $A^{2}\Sigma^{+}$  state of OH is crossed by three repulsive electronic states that dissociate to the atomic fragments  $O({}^{3}P_{i})$ +H(<sup>2</sup>S). These repulsive  ${}^{4}\Sigma^{-}$ ,  ${}^{2}\Sigma^{-}$ , and  ${}^{4}\Pi$  states are coupled to the bound A  ${}^{2}\Sigma^{+}$  state via spin-orbit couplings, and the extent to which these states affect the predissociation rate varies with the vibrational level of the OH A  $^{2}\Sigma^{+}$  and the rotational quantum number; for example, for OH A  $^{2}\Sigma^{+}$ , v'=3 rates are  $0.33 \times 10^{10} \text{ s}^{-1}$  for N'=0 and 1.58  $\times 10^{10}$  s<sup>-1</sup> for N' = 14, with rates for *e*-parity (F<sub>1</sub>) levels up to 10% higher than for f-parity ( $F_2$ ) levels. Recent Fermi Golden Rule calculations of the predissociation rates of OH  $A^{2}\Sigma^{+}$ , v', N' levels employing *ab initio* electronic wave functions for the A  ${}^{2}\Sigma^{+}$ ,  ${}^{4}\Sigma^{-}$ ,  ${}^{2}\Sigma^{-}$ , and  ${}^{4}\Pi$  states and computed values of the spin-orbit coupling between these states

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showed excellent agreement with the available experimental data.28

The SH A  ${}^{2}\Sigma^{+}$  state is similarly crossed by  ${}^{4}\Sigma^{-}$ ,  ${}^{2}\Sigma^{-}$ , and <sup>4</sup> $\Pi$  repulsive states that correlate with S(<sup>3</sup> $P_i$ ) and H(<sup>2</sup>S) at large internuclear separation. Riad Manaa<sup>24</sup> performed detailed ab initio electronic structure calculations of the potential energy curves for all four of these states and for the spin-orbit and Coriolis couplings between the states. Predissociation rates based on these ab initio results were not, however, calculated. The experimental data with which to compare such calculated rates has, until now, been sparse, and measurement of accurate lifetimes for SH and SD A  ${}^{2}\Sigma^{+}, v', N'$  levels has been restricted to  $v' = 0.{}^{10,18-21}$  A comparison of predissociation rates of SH A  ${}^{2}\Sigma^{+}$  with the much-studied OH A  ${}^{2}\Sigma^{+}$  should highlight the effects of the different spin-orbit interactions in these first- and secondrow hydride radicals.

The technique of cavity ring-down spectroscopy (CRDS)<sup>29-31</sup> enables spectroscopic probing of the predissociated v', N' levels of SH and SD  $A^2\Sigma^+$  for v' > 0 because it is a direct absorption technique and because the high sensitivity of CRDS allows measurement of SH and SD spectra at low pressures where collision-induced broadening is negligible. We have recently demonstrated the power of CRDS for studies of molecular predissociations in which the lifetimes of the predissociated states are less than  $\sim$  500 ps.<sup>32</sup> CRDS therefore provides a complementary method to LIF which is better suited to study the decay of longer-lived states. In an earlier communication,<sup>33</sup> we reported a highresolution cavity ring-down spectrum of the A  ${}^{2}\Sigma^{+}-X^{2}\Pi$ (1,0) band of SH. From the accurately determined spectral linewidths, we extracted predissociation rates for SH A  $^{2}\Sigma^{+}$ , v'=1, N'=0-8 and compared the experimental data with Fermi Golden Rule calculations using a combination of the ab initio spin-orbit coupling values and repulsive state potentials of Riad Manaa<sup>24</sup> and a potential for the A  ${}^{2}\Sigma^{+}$  state obtained from spectroscopic and photochemical data. The calculated and measured predissociation rates were in quantitative agreement. In this paper we extend this work to present the cavity ring-down spectra of the SD  $A^{2}\Sigma^{+}-X^{2}\Pi$  (1,0) and (2,0) bands. From the CRD spectra we determine predissociation rates which we compare to Fermi Golden Rule calculations using the same potentials and coupling functions. As a further test of our theoretical model, we calculate the variation of the predissociation rates with N' for SH and SD A  ${}^{2}\Sigma^{+}$  v'=0 and compare the results with previous experimental studies. The result is a unified experimental and theoretical picture of the mechanism of predissociation of SH/SD A  ${}^{2}\Sigma^{+}$   $v' \leq 2$ , as well as predictions for the predissociative behavior of higher v' levels.

#### **II. EXPERIMENT**

The cavity ring-down spectroscopy apparatus used to record spectra of the SH and SD A-X bands consists of a pulsed dye laser system, a glass flow tube bounded by high reflectivity mirrors, signal detection and acquisition electronics, and wavelength calibration equipment.

The 532 nm output of a Nd:YAG (Quantel YG680) laser was used to pump a dye laser (Spectra Physics PDL-3) operating with DCM and Rhodamine 610 dyes. The dye laser output energy was typically  $\sim$  30 mJ and had a bandwidth of  $\sim 0.07 \text{ cm}^{-1}$ . Part of the dye laser fundamental was separated from the main laser beam using a quartz flat and directed into an iodine LIF cell and an étalon (free spectral range  $0.492 \text{ cm}^{-1}$ ) for accurate wavelength calibration. The standard deviations of fits to the well-documented I<sub>2</sub> B-Xspectra<sup>34</sup> and étalon fringes were  $< 0.01 \text{ cm}^{-1}$ . The remaining laser beam was frequency doubled in a KDP crystal housed in a homebuilt autotracker and the residual fundamental light was removed using a filter. The resultant UV beam had an energy of 3-6 mJ per pulse and was injected into the ring-down cavity (RDC) through one of the cavity end mirrors. The UV mirrors (Research Electro-Optics, 7.75 mm diam, 4 mm thick quartz substrates) had a specified reflectivity of >99.9% at 320 nm and a 2 m radius of curvature. They were mounted 1.6 m apart in PTFE disks connected to the glass flow cell by flexible bellows. Fine control of the mirror positions was achieved using micrometer screws located alongside the bellows, and mirror alignment was assisted by a helium-neon laser. Light escaping from the RDC was detected by a photomultiplier (EMI 9592) mounted behind one of the mirrors. Background fluorescence arising from the UV laser beam passing through the mirror substrates was eliminated by a filter placed in front of the PMT. The signal from the PMT was digitized using a digital oscilloscope (LeCroy 9400) and transferred to a PC via a GPIB interface for analysis. Care was taken to ensure that the ring-down signal was a single-exponential decay. Ringdown times (1/e) were typically  $\sim 10 \ \mu s$  at 306 nm. Spectra were recorded by monitoring the variation of the ring-down time with wavelength.

The flow tube consisted of a 25 mm diam glass tube with several ports along its length for pressure gauges and gas inlets. The flow tube was evacuated by a rotary pump (Edwards) connected close to one end of the tube by a vibrationisolating bellows. The pressure in the cell was monitored by capacitance manometer gauges (0-10 and 0-1000 Torr) and could be regulated using a throttling valve before the rotary pump. SH was formed in a continuous flow via the reaction of hydrogen atoms with H<sub>2</sub>S. The hydrogen atoms were formed by microwave discharge of H<sub>2</sub> (BOC High Purity) in a phosphoric-acid coated mullite tube (10 cm long, 12 mm o.d.) and were introduced to the RDC 33 cm from one end; they reacted in the RDC with a few mTorr of H<sub>2</sub>S (Matheson, 99.5% purity) introduced further upstream. Typical pressures of H<sub>2</sub> in the discharge were 0.5-1.0 Torr and the microwave discharge operated at  $\sim$  50 W input power. Careful control of the gas mixes using needle valves suppressed the formation of  $S_2$  which was observed as a by-product of the reaction to form the SH. Measurement of the widths of nonpredissociated lines in the S<sub>2</sub> B-X spectrum<sup>35</sup> in the wavelength region of the SH experiments established the UV laser linewidth in our experiments as 0.09 cm<sup>-1</sup> FWHM, with the line shape well described by a Gaussian function.



FIG. 1. Experimental (bottom) and simulated (top) spectra of part of the SH  $A^{2}\Sigma^{+}-X^{2}\Pi$  (1,0) band, with rotational line assignments indicated by the combs above the spectra. The simulation was performed using spectroscopic constants from Refs. 9 and 38 and assumes a temperature of 300 K. The line shapes in the simulation are a convolution of a Gaussian (FWHM 0.09 cm<sup>-1</sup>) and a Lorentzian (FWHM 1.0 cm<sup>-1</sup>) function.

SD was produced by the reaction of  $D_2S$  with D atoms formed from a microwave discharge in  $D_2$  (Spectra Gases, Research Grade) under the conditions described above.  $D_2S$ was synthesised by the reaction of  $D_3PO_4$  in  $D_2O$  with FeS in a deuterated vacuum line and was stored in a 5  $\ell$  glass bulb. Prior to studying SD, the entire vacuum apparatus was deuterated by overnight exposure to  $D_2O$ , and the microwave discharge tube was coated with deuterated phosphoric acid. Although the reaction of H atoms with  $D_2S$  should produce SD cleanly, the reaction with D atoms was found to give better SD signal with less SH contamination.

The experimental design precludes any detrimental effects of cavity modes on our spectra.<sup>36,37</sup> The longitudinal mode spacing of the RDC is calculated to be 0.003 cm<sup>-1</sup>, much narrower than either the laser bandwidth or the widths of the spectral features under investigation. The lifetimes for SH and SD A  ${}^{2}\Sigma^{+}$ , as discussed below, are shorter than the cavity round trip time of the laser pulse (~10 ns), so coherent effects of multiple pulses interacting with the SH/SD excited state can be neglected. The short lifetimes of the SH and SD A-state levels also mean that the spectral linewidths are greater than the laser bandwidth, thereby ensuring that conditions appropriate to Beer–Lambert law absorption are satisfied.

# **III. RESULTS**

Spectra were recorded of the SH  $A^{2}\Sigma^{+}-X^{2}\Pi$  (1,0) band and of the SD  $A^{2}\Sigma^{+}-X^{2}\Pi$  (1,0) and (2,0) bands, all of which fall in the wavelength range 298–317 nm. Attempts

to record the SH A - X (2,0) band were foiled by a combination of poor Franck-Condon factors for the transition, the likely very large lifetime broadening of the spectral lines, and the strong overlapping S<sub>2</sub> B  ${}^{3}\Sigma_{\mu}^{-} - X {}^{3}\Sigma_{\rho}^{-}$  (6,0) band that could not be eliminated by adjustment of the H<sub>2</sub>S: H atom mixing ratio. In addition, the reflectivities of our mirror sets at the wavelengths appropriate to the (2,0) band were substantially less than the maximum mirror reflectivity and the maximum ring-down time observed at 290 nm was 4  $\mu$ s. Figure 1 shows the CRDS spectrum of the SH A  ${}^{2}\Sigma^{+}-X {}^{2}\Pi$ (1,0) band over the wavenumber range 32 390-32 670 cm<sup>-1</sup> together with a simulation derived using the literature values for the ground<sup>38</sup> and excited<sup>9,18</sup> states. The simulation assumes a temperature of 300 K, a Gaussian instrument function of FWHM 0.09 cm<sup>-1</sup>, and a Lorentzian component of the line profile of FWHM 1.0 cm<sup>-1</sup> to allow for homogeneous lifetime broadening. The simulation reproduces the observed positions, intensities and widths of the spectral lines very well, but to interpret the effects of predissociation as precisely as possible, we fitted unblended spectral lines as described below to determine accurately the homogeneous widths of individual rotational levels.

The excited states of SH (SD) can, in principle, decay via two routes, radiative decay and predissociation. If the rate constants for these two processes are denoted as  $k_{\rm rad}$  and  $k_{\rm pre}$ , respectively, the total rate of decay of the excited state is determined by an overall rate constant  $k=k_{\rm rad}+k_{\rm pre}$ . The natural lifetime of the excited state,  $\tau(=1/k)$  is related to the

TABLE I. SH A  ${}^{2}\Sigma^{+}$  v' = 1, N' lifetimes. Error limits in the quoted lifetimes correspond to  $2\sigma$  in the fit of the experimental linewidths.

	Lifetime/ps			
N'	e parity	f parity		
0	$5.45^{+0.24}_{-0.22}$			
1	$5.45^{+0.24}_{-0.22}$			
2				
3	$4.93^{+0.36}_{-0.32}$	$5.10^{+0.36}_{-0.32}$		
4	$5.19_{-0.33}^{+0.37}$	$4.64_{-0.42}^{+0.51}$		
5	$4.97_{-0.25}^{+0.25}$	$4.70^{+0.65}_{-0.51}$		
6	$4.65_{-0.27}^{+0.31}$	$4.08^{+0.27}_{-0.24}$		
7	$4.59^{+0.42}_{-0.36}$	0.21		
8	$4.61_{-0.55}^{+0.73}$			



associated radiative and predissociative lifetimes,  $au_{\rm rad}$  and  $\tau_{\rm pre}$ , respectively, via

$$\frac{1}{\tau} = \frac{1}{\tau_{\rm rad}} + \frac{1}{\tau_{\rm pre}}.$$
(1)

The deduced radiative lifetimes of SH A  ${}^{2}\Sigma^{+}v'=0$  and SD  $A^{2}\Sigma^{+}v'=0$  are of the order of 700–800 ns,<sup>10</sup> whereas the natural lifetimes measured in this study are less than 100 ps. Since it is reasonable to assume only a small R-dependence in the A-X electronic transition moment and thus a small v'-dependence to the radiative lifetime of the A state, we can thus safely equate the measured natural lifetimes with the predissociative lifetimes of the A  ${}^{2}\Sigma^{+} v' > 0$  levels. As described previously,  ${}^{32,33}$  homogeneous contributions

to the widths of spectral lines were determined by fitting unblended spectral lines to a Voigt profile. The Voigt profile is a convolution of a Gaussian function (corresponding to the combined effects of the laser line shape and Doppler broadening) and a Lorentzian function (corresponding to the effects of lifetime broadening). The FWHM of the Gaussian function is determined by fitting  $S_2$  transitions that overlap the SH and SD spectra. Although the Doppler components due to SH and  $S_2$  will differ slightly, the bandwidth of the UV laser beam dominates the Gaussian "instrument" function and we determine a FWHM of  $0.09 \text{ cm}^{-1}$  that we attribute primarily to the laser bandwidth. This Gaussian contribution to the Voigt profile is held fixed during the line fitting, and this fitting then determines the FWHM of the Lorentzian component,  $\Gamma$ . The homogeneous linewidths are related to the natural lifetimes by

$$\Gamma(\mathrm{cm}^{-1}) = \frac{1}{2 \,\pi c \,\tau}.\tag{2}$$

The results of this fitting process are listed in Table I for SH  $A^{2}\Sigma^{+}$ , v'=1, N'=0-8. Within the errors of the measurements, we observe no difference in predissociation rates for the e- and f-parity rotational levels of v'=1. The fitting assumes that unresolved hyperfine structure and pressure broadening make negligible contributions to the lineshapes. Hyperfine splittings of  $< 0.03 \text{ cm}^{-1}$  have been measured<sup>18</sup> for SH A  ${}^{2}\Sigma^{+}$  v' = 0, N' = 14 while, at the pressures of <1

FIG. 2. Experimental (bottom) and simulated (top) spectra of part of the SD  $A^{2}\Sigma^{+}-X^{2}\Pi$  (1,0) band, with rotational line assignments indicated by the comb above the spectra. The simulation was performed using spectroscopic constants from Refs. 9, 12, and 39 and assumes a temperature of 300 K. The line shapes in the simulation are a convolution of a Gaussian (FWHM 0.09 cm<sup>-1</sup>) and a Lorentzian (FWHM 0.14 cm<sup>-1</sup>) function.

Torr used in our experiments, pressure broadening is expected to result in a linewidth contribution of  $< 0.001 \text{ cm}^{-1}$ .

Figure 2 shows a portion of the spectrum of the SD  $A^{2}\Sigma^{+}-X^{2}\Pi$  (1,0) band in the wavenumber range  $32\ 310-32\ 350\ \text{cm}^{-1}$ . The signal to noise ratio in this spectrum is worse than in the equivalent SH band, presumably because of the less efficient production of SD in our discharge flow system. Shown with the experimental spectrum is a simulated spectrum calculated using the spectroscopic constants for SD in its  $X^{2}\Pi$  and  $A^{2}\Sigma^{+}$  states.<sup>9,12,39</sup> The closest correspondence between the observed and measured line shapes is obtained if the 0.09 cm<sup>-1</sup> FWHM Gaussian instrument function is convoluted with a Lorentzian profile of  $\Gamma = 0.14 \text{ cm}^{-1}$  (FWHM). This homogeneous broadening is equivalent to an upper state lifetime of  $\sim 30$  ps. The signal to noise ratio and the modest homogeneous broadening prevent accurate fitting of unblended spectral lines to determine the N' dependence of the predissociation rate. The linewidths are virtually at the limit we can determine reproducibly with our UV laser bandwidth and hence we restrict ourselves to the observation that the lifetimes of the SD A  $^{2}\Sigma^{+}$ v' = 1 rotational levels are  $\geq 30$  ps.

As mentioned above, we were unable to record spectra of the SH A-X (2,0) band because of a combination of unfavorable factors. We were, however, successful in observing portions of the SD A - X (2,0) band and part of this spectrum in the wavenumber range  $33 430-33 520 \text{ cm}^{-1}$  is shown in Fig. 3. The figure also shows a simulation of the band calculated as described above and including a homogeneous contribution to the spectral line shapes with  $\Gamma = 2.3 \text{ cm}^{-1}$ FWHM. This value of  $\Gamma$  was determined by fitting the complete experimental spectrum to a simulation with the linewidth as a floated parameter. The spectrum is overlapped by a band of the S<sub>2</sub> B-X transition, and much of the apparent "noise" in the spectrum is in fact sharp, unbroadened S<sub>2</sub> spectral lines. The procedure used to determine  $\Gamma$  precludes



FIG. 3. Experimental (bottom) and simulated (top) spectra of part of the SD  $A^{2}\Sigma^{+}-X^{2}\Pi$  (2,0) band, with rotational line assignments indicated by the combs above the spectra. The simulation was performed using spectroscopic constants from Refs. 9, 12, and 39 and assumes a temperature of 300 K. The Lorentzian component of the line shapes in the simulation was floated as a variable parameter in a fit to the experimental spectrum, giving a FWHM of 2.3 cm<sup>-1</sup>. As in previous figures, the Gaussian component of the line shape was fixed with FWHM 0.09 cm<sup>-1</sup>. The sharp features in the experimental spectrum are overlapping rotational lines of the S<sub>2</sub> *B*-*X* transition.

measurement of the N' dependence of the predissociation rate from SD A  ${}^{2}\Sigma^{+}v'=2$ . Direct fitting of "single" lines to establish this N' dependence is not feasible because the widths of the features mean there are in fact no isolated lines in the spectrum. A value of  $\Gamma = 2.3 \text{ cm}^{-1}$  corresponds to a SD A  ${}^{2}\Sigma^{+}v'=2$  lifetime of 2.3 ps.

In Table II we have collected together all the available experimental information on SH and SD  $A^{2}\Sigma^{+}v'$  predissociative lifetimes. The variation of the predissociation rate with v' and with hydrogen isotope can be understood in terms of the proximity of the vibrational energy levels of the  $A^{2}\Sigma^{+}$  state to the crossing points of the  $A^{2}\Sigma^{+}$  and repulsive  ${}^{4}\Sigma^{-}$ ,  ${}^{2}\Sigma^{-}$ , and  ${}^{4}\Pi$  potentials. This point will be addressed in more detail in Sec. V.

# **IV. CALCULATIONS**

The availability in the literature of *ab initio* potentials for the various electronic states of SH and for the *R*-dependence of the spin-orbit coupling between the electronic states has permitted us to perform detailed calculations of the rates of predissociation of individual v', N' levels of SH and SD  $A^{2}\Sigma^{+}$  and to compare these calculations with our experimental data. The results of this analysis clarify the

TABLE II. Summary of the variation of SH/SD A  ${}^{2}\Sigma^{+} v'$  lifetimes for experimentally observed levels typically over the range  $N' \approx 0-10$ .

	Lifeti	ime
υ'	SH	SD
0	3.20-0.95 ns <sup>a</sup>	247–38 ns <sup>b</sup>
1	5.45-4.61 ps	35–24 ps
2		2.31 ps

<sup>b</sup>Taken from Ref. 21.

relative roles of the different repulsive states in the predissociation mechanism and make apparent the origins of the observed variations of the predissociation rates with v' and N'for this system. The calculations neglect the effects of the parity of the rotational levels but we will return to this point later.

Predissociation rates were calculated using a slightly modified version of the program BCONT.<sup>40</sup> The program requires potential functions for the bound and repulsive states involved in the predissociation mechanism and the relevant functions are taken from a combination of *ab initio* calculations and experimental data. The first three dissociative states, the  $1^{4}\Sigma^{-}$ ,  $1^{2}\Sigma^{-}$ , and  $1^{4}\Pi$  states, arise (predominantly) from the electron configurations

$$..3\sigma^{2}1\pi^{4}4\sigma^{2}5\sigma^{2}6\sigma^{1}2\pi^{2}; \quad 1\ {}^{4}\Sigma^{-}, 1\ {}^{2}\Sigma$$
$$..3\sigma^{2}1\pi^{4}4\sigma^{2}5\sigma^{1}6\sigma^{1}2\pi^{3}; \quad 1\ {}^{4}\Pi,$$

and the only available information about the form of these dissociative potentials comes from *ab initio* calculations. In this work, we make use of the results of the most recent of these *ab initio* studies of the potential energy functions<sup>24</sup> which are calculated to cross the outer limb of the (*ab initio*)  $A^{2}\Sigma^{+}$  state potential at  $R_{c}(1^{4}\Sigma^{-})=1.71$  Å,  $R_{c}(1^{2}\Sigma^{-})=1.90$  Å, and  $R_{c}(1^{4}\Pi)=2.04$  Å, respectively. We fit the *ab initio* repulsive potentials to analytic functions of the form

$$V_{\rm rep}(R) = D + A \exp\{-[b_1(R - R_x) + b_2(R - R_x)^2]\}, \qquad (3)$$

where *D*, the energy at the potential asymptote was fixed at  $-564 \text{ cm}^{-1}$ , measured relative to the *A* state minimum, so as to be in agreement with the known<sup>41</sup> asymptotic splitting between the <sup>1</sup>*D* and <sup>3</sup>*P*<sub>2</sub> states of atomic sulphur (9239 cm<sup>-1</sup>). *A*, *b*<sub>1</sub>, and *b*<sub>2</sub> are fitted parameters, and *R*<sub>x</sub> defines the S–H bond length about which we expand the potential. The choice of *R*<sub>x</sub> is arbitrary (but determines the fitted values of the remaining parameters) and was initially chosen to be the *ab initio* value for the crossing point, *R*<sub>c</sub>. Once the repulsive potentials are fitted to functions of the form of Eq. (3), however, the value of *R*<sub>x</sub> can be adjusted to move the whole potential function to longer or shorter *R* as a means of varying the crossing point energy and internuclear separation.

The *ab initio* potential for the  $A^{2}\Sigma^{+}$  state proved too inaccurate for the purposes of our calculation since it did not reproduce the known vibrational frequencies and energies of SH (SD) nor does it asymptotically give the correct energy of S(<sup>1</sup>D) relative to S(<sup>3</sup>P). Consequently, we chose to fit available experimental data to obtain a more accurate A-state potential. We used two sources of experimental data; the results of 121.6 nm photolysis of H<sub>2</sub>S (and D<sub>2</sub>S)<sup>42,43</sup> and of rotationally and vibrationally resolved spectroscopic studies of the A-X transitions of SH and SD.<sup>8,9</sup> The former experiments established the well depth,  $D_e$ , of the bound  $A^{2}\Sigma^{+}$ state potential as  $-8675\pm100$  cm<sup>-1</sup> [relative to the asymptotic products H+S(<sup>1</sup>D<sub>2</sub>)] as well as the energies of several SH (SD)  $A^{2}\Sigma^{+}$  v' levels not observed in



FIG. 4. Potential energy curves used in the calculations of SH and SD A  $^{2}\Sigma^{+}$  predissociation rates. The horizontal lines show the energies of the vibrational levels of the  $A^{2}\Sigma^{+}$  states of SH (left) and SD (right). The zero of energy is defined as the minimum of the  $A^{2}\Sigma^{+}$  state potential.

absorption spectroscopy. The A-state potential energy curve was constructed using an extended Rydberg function<sup>44</sup>

$$V(R) = -D_e(1 + a_1\rho + a_2\rho^2)\exp(-a_1\rho), \qquad (4)$$

where  $\rho = R - R_e$ , the distortion from the equilibrium bond length ( $R_e = 1.423$  Å) and  $a_1$  and  $a_2$  are fitted parameters describing the shape of the potential. We refitted the previously tabulated experimental data for both SH and SD, simultaneously, to yield the following unified values of the parameters,  $a_1 = 2.90 \text{ Å}^{-1}$ ,  $a_2 = -2.33 \text{ Å}^{-2}$ , using a suitably modified version of the program LEVEL.<sup>45</sup> This program solves the one-dimensional Schrödinger equation for a chosen potential and minimises the squares of the residuals between the observed and calculated term values. The A-state potential used in subsequent calculations reported in this paper was shifted upwards in energy by  $D_e$  so that the reference zero of energy for all potential functions is taken as the bottom of the A-state well.

Figure 4 shows the bound A  ${}^{2}\Sigma^{+}$  and repulsive 1  ${}^{4}\Sigma^{-}$ .  $1^{2}\Sigma^{-}$ , and  $1^{4}\Pi$  potentials used in the subsequent analysis, along with the calculated vibrational levels of the A state for SH and SD. From this picture it is apparent that the most significant contribution to the predissociation rate of low v'levels of the A state is likely to be from interaction with the  $1^{4}\Sigma^{-}$  state. A similar interaction has been invoked as the main contributor to the predissociation of low v' levels of the corresponding  $A^{2}\Sigma^{+}$  states of both OH and OD.<sup>28</sup> To quantify the contributions to the predissociation from the three different repulsive states,  $1^{4}\Sigma^{-}$ ,  $1^{2}\Sigma^{-}$ , and  $1^{4}\Pi$ , we have taken the calculated spin-orbit coupling matrix elements  $H^{SO}(A^{2}\Sigma^{+}, 1^{4}\Sigma^{-}), H^{SO}(A^{2}\Sigma^{+}, 1^{2}\Sigma^{-}),$ and  $H^{SO}(A^{2}\Sigma^{+}, 1^{4}\Pi)$  which are a sensitive function of S-H bond length in the region of the respective crossing points.<sup>24</sup> We parameterized these matrix elements as a Taylor expansion in the shifted distance coordinate,  $(R - R_x)$ , to yield an effective coupling function  $H^{SO}(R)$ ,

$$H^{SO}(R) = m_0 + m_1(R - R_x) + m_2(R - R_x)^2.$$
 (5)

The values of all parameters required for Eqs. (4) and (5) are listed in Table III. Having set up the potentials we calculated the bound,  $\langle v, N \rangle$ , and continuum,  $\langle E, N \rangle$ , wave functions using the program BCONT<sup>40</sup> to solve the radial Schrödinger equation and determine the matrix elements,

$$H^{\rm SO}(E,N;v,N) = \langle E,N | H^{\rm SO}(R) | v,N \rangle.$$
(6)

The final stage of the calculation is to use the Fermi Golden Rule approximation to evaluate the predissociation rates of the v', N' levels of the A state. The rate constant for predissociation of a particular v', N' level with energy E is calculated using

$$k(v',N') = (4\pi^2 G_{\rm el}/h) |\langle E,N'| H^{\rm SO}(R) |v',N'\rangle|^2.$$
(7)

Here,  $G_{\rm el}$  is the ratio of electronic degeneracy factors of the final and initial states.

Predissociation rates were calculated, as a function of the bound state v' and N' quantum numbers, for interaction with each of the three repulsive curves. As expected, the rates obtained for the SH and SD A  ${}^{2}\Sigma^{+}$   $v' \leq 1$  levels interacting with the higher lying  $1^{2}\Sigma^{-}$  and  $1^{4}\Pi$  states were several orders of magnitude smaller than those from interaction with the 1  ${}^{4}\Sigma^{-}$  state. For SD A  ${}^{2}\Sigma^{+}$  v'=2 the rates of predissociation via the 1  $^2\Sigma^-$  and 1  $^4\Pi$  states are calculated to be  $10^3$  and  $10^5$  times slower than for predissociation via the 1  ${}^{4}\Sigma^{-}$  state, but for SH A  ${}^{2}\Sigma^{+}$  v'=2 the corresponding

TABLE III. Parameters for the potentials and coupling functions used in the calculations of the SH/SD A  ${}^{2}\Sigma^{+}v',N'$  predissociation rates. All parameters are defined in the text.

	$b_1$ /Å <sup>-1</sup>	$b_2$ /Å <sup>-2</sup>	$D / cm^{-1}$	$A / cm^{-1}$	$R_x$ /Å	$m_0 / \mathrm{cm}^{-1}$	$m_1 / \text{Å}^{-1} \text{ cm}^{-1}$	$/{\rm \AA}^{-2} {\rm ~cm}^{-1}$
$1^{4}\Sigma^{-}$	3.26	0.13	- 564	4626.17	1.68	44	140	60
$1^{2}\Sigma^{-}$	2.20	0.17	-564	6730.83	1.87	50	109	-37
1 <sup>4</sup> Π	2.53	0.27	- 564	8494.46	2.00	-162	67	54

rates are both only one order of magnitude slower, suggesting the onset of significant predissociation via routes other than crossing to the  $1 \, {}^{4}\Sigma^{-}$  potential.

Figures 5–9 show a comparison of the calculated and experimental predissociation lifetimes for SH  $A^2\Sigma^+ v' = 0,1$  and SD  $A^2\Sigma^+ v' = 0,1,2$ . The experimental data in Figs. 5 and 7 are from Ubachs *et al.*<sup>18,19</sup> and Kawasaki *et al.*,<sup>21</sup> respectively. The data for SD v'=0 has been converted from fluorescence lifetimes to predissociative lifetimes using the known radiative lifetime of SD  $A^2\Sigma^+$ .<sup>10</sup>

The calculated data were obtained as described above after optimization of the repulsive potentials to give the shown match with the N'-dependent SH A  $^{2}\Sigma^{+}v'=1$  experimental data. This optimization was done in a trial-anderror fashion by making minor adjustments to the  $1^{4}\Sigma^{-1}$ state potential from which we find, by inspection, that the experimentally measured SH (A)v' = 1 lifetimes are reproduced best if the whole  $1 \, {}^{4}\Sigma^{-}$  state potential is shifted by -0.03 Å from the *ab initio* value, i.e., if  $R_x$  is decreased from 1.71 Å to 1.68 Å. This new value of  $R_{y}$  is also used in Eq. (5) for the coupling function. The crossing point of the  $A^{2}\Sigma^{+}$  and  $1^{4}\Sigma^{-}$  potentials then occurs at  $R_{c} = 1.75$  Å. The repulsive potentials shown in Fig. 4 are all shifted inwards by 0.03 Å from their *ab initio* crossing points with the A state, and all other calculated results displayed in Figs. 5-9 make use of these slightly shifted *ab initio*  $1^{4}\Sigma^{-}$ ,  $1^{2}\Sigma^{-}$ , and  $1^{4}\Pi$  potentials and coupling functions and were not optimised for each experimental data set. The potentials



FIG. 5. Lifetimes of SH  $A^{2}\Sigma^{+}v'=0$ . Experimental results are shown by circles,  $\bullet$ ; *e* parity,  $\bigcirc$ ; *f* parity; diamonds are the results of calculations described in the text. Experimental data are taken from Refs. 18 and 19.

and coupling functions we have chosen for the calculations are probably not unique in being able to model the experimental data but, as is apparent from the figures, the agreement between experiment and calculations for all data sets is excellent. The calculations for SH and SD match not just the absolute rates and lifetimes for different v' states, which vary by about five orders of magnitude, but also reproduce the N' dependence for the different v'. The greatest discrepancies are for SD v'=1 but, as pointed out in Sec. III, the linewidths in the SD A-X(1,0) band are very close to our experimental instrument function so precise determination of the homogeneous contributions to the linewidths is particularly difficult for this transition.

### **V. DISCUSSION**

We are now in a position to compare the variation of the predissociation rates of SH and SD  $A^{2}\Sigma^{+}$  with hydrogen isotope and with vibrational and rotational level. The calculations described in the previous section reproduce quantitatively the magnitudes and variation of these rates and we can use the potentials, energy levels and wave functions from the calculations to interpret our experimental observations and to make predictions about the predissociation for levels with v' > 2.

The predissociation rate for a particular state depends on the extent of overlap of the bound state and continuum wave functions<sup>46</sup> and this overlap will be greatest for energy levels



FIG. 6. Lifetimes of SH A  ${}^{2}\Sigma^{+} v' = 1$ . Experimental results are shown by circles,  $\bullet$ ; *e* parity,  $\bigcirc$ ; *f* parity; diamonds are the results of calculations described in the text.



FIG. 7. Lifetimes of SD A  ${}^{2}\Sigma^{+} v' = 0$ . Experimental results are shown by circles,  $\bullet$ ; *e* parity,  $\bigcirc$ ; *f* parity; diamonds are the results of calculations described in the text. Experimental data are taken from Ref. 21.

in close proximity to the energy of the crossing point between the  $A^{2}\Sigma^{+}$  and repulsive-state potentials. The variation of the predissociation rate with v' is summarized in Table II, and Fig. 4 shows a plot of the potentials for the  $A^{2}\Sigma^{+}$ ,  $1^{4}\Sigma^{-}$ ,  $1^{2}\Sigma^{-}$ , and  $1^{4}\Pi$  states used in the calculations. These calculations demonstrate that the predissociation of the v'=0,1, and 2 levels is dominated both for SH and SD by crossing to the  $1^{4}\Sigma^{-}$  state and it is clear from the figure that the large increase in predissociation rate for SH as v'increases from 0 to 1 is caused by the closeness of v'=1 to



FIG. 8. Calculated lifetimes of SD  $A^{2}\Sigma^{+}v'=1$  (top) and SD  $A^{2}\Sigma^{+}v'=2$  (bottom). For reasons outlined in the text we were unable to give an experimental variation of lifetime with N' for these vibrational levels. SD  $A^{2}\Sigma^{+}v'=1$  has an experimentally measured lifetime of ~30 ps whilst that for SD  $A^{2}\Sigma^{+}v'=2$  is 2.3 ps.



FIG. 9. Calculated bound ( $A^{2}\Sigma^{+}$ ) and continuum ( $1^{4}\Sigma^{-}$ ) nuclear radial wave functions for SD. The bottom panel shows the SD  $A^{2}\Sigma^{+}v'=0$  wave function and the  $1^{4}\Sigma^{-}$  wave function of the same energy. The top panel shows the SD  $A^{2}\Sigma^{+}v'=2$  wave function and the  $1^{4}\Sigma^{-}$  wave function of the same energy.

the energy of the crossing. Likewise, because of isotopic effects, the vibrational levels of SD lie lower in the potential than those of SH with the same vibrational quantum number. Hence, we observe a faster predissociation for SH v'=1than for SD v'=1. The energy of SD v'=2, however, is greater than that of SH v' = 1 and the former state predissociates about twice as quickly as the latter. Our calculations of the rate for predissociation of SD v' = 2 predict a lifetime of  $\sim 2.3$  ps in extraordinarily good agreement with the experimental result. To illustrate the influence of the overlap of the bound (A  ${}^{2}\Sigma^{+}$ ) and continuum (1  ${}^{4}\Sigma^{-}$ ) nuclear radial wave functions on the predissociation rate, Fig. 9 shows plots of the calculated SD A  $^{2}\Sigma^{+}$  v'=0 and v'=2 wave functions together with continuum wave functions of the same energy; it is evident that proximity to the crossing of the A  ${}^{2}\Sigma^{+}$  and  $1\ ^{4}\Sigma^{-}$  potentials substantially enhances this overlap in the latter case.

No experimental lifetime data exist for either SH or SD for levels v' > 2 with which to make a comparison to this model. However, from a purely theoretical point of view it is still interesting to see what predictions can be made for these higher vibrational levels in order to understand the roles of the  ${}^{2}\Sigma^{-}$  and  ${}^{4}\Pi$  dissociative states (also shifted inwards by -0.03 Å from their *ab initio* values and assuming the calculated<sup>24</sup> values of the spin–orbit coupling matrix elements). For levels with  $v' \leq 2$  the dominant predissociation route is via the  ${}^{4}\Sigma^{-}$  state as already mentioned in the previous section. However, for higher vibrational levels the  ${}^{4}\Pi$ 



FIG. 10. Variation of predissociation rate with each individual dissociative state and the total predissociation rate for the first six vibrational levels of SH  $A^{2}\Sigma^{+}$ .

state rapidly becomes the main predissociation channel whilst the  ${}^{2}\Sigma^{-}$  state only ever seems to play a minor role. This point is illustrated in Fig. 10 which shows the calculated predissociation rates of SH (*A*) via each individual channel as well as the total rate plotted against the rotationless levels of v' = 0-5. The total rate reported here is simply a summation of the three individual rates from a given v' level

Our calculations also reveal the origins of the rotational dependence of the lifetimes of SH v'=0,1 and SD v'=0. The bound and continuum wavefunctions are solutions of the radial Schrödinger equation and, for N'>0, the potential is modified by addition of a centrifugal term giving

$$-\frac{\hbar^2}{2\mu}\frac{d^2\Psi}{dR^2} + \left[V(R) + \frac{\hbar^2}{2\mu}\frac{N'(N'+1)}{R^2}\right]\Psi = E\Psi.$$
 (8)

The vibrational and continuum wave functions and the overlap between them thus depend implicitly on the rotational quantum number and this variation in the overlap with N'gives the observed N' dependence of the predissociation rate. Our calculations show that for vibrational levels lower in energy than the crossing point of the bound and repulsive potentials, the predissociation rate increases with increasing molecular rotation, whereas for vibrational levels lying above the crossing point, e.g., SH(v'=2), the effect of increased rotation is to decrease the predissociation rate.

The calculations neglect the effect of parity of the rotational levels on the predissociation rate. The experimental data of Ubachs *et al.*<sup>18,19</sup> for SH v'=0 and of Kawasaki *et al.*<sup>21</sup> for SD v'=0 show a small but significant difference in the rates of predissociation for the two parities, with *e*-parity levels having slightly shorter lifetimes than *f*-parity levels. Similar effects have been observed for the predissociation of OH  $A^{2}\Sigma^{+}$  in several vibrational levels, and calculations of the predissociation rates for OH reproduce this difference. The effect in OH is attributed to the nature of the angular momentum coupling in the repulsive  $1^{4}\Sigma^{-}$  state; if the coupling is pure Hund's case (b) the *e*-parity levels are predicted to show faster predissociation than the *f*-levels, while for case (a) coupling the reverse is true.<sup>27</sup> For OH predissociation by the <sup>4</sup> $\Pi$  state, the calculations suggested little or no variation with e/f parity. For SH v' = 1, we observe no significant difference between the predissociation rates of e and f-parity levels.

The other possible source of differences in the predissociation rates for the *e* and *f*-parity rotational levels is the difference in energy. For SH or SD  $A^{2}\Sigma^{+}$  the *e*-parity level lies slightly higher in energy than the *f*-parity level of the same N' quantum number. We have investigated the effect of this very small energy shift on the calculated predissociation rates and find it to be negligible.

It is interesting to compare the lifetime data for the *A* states of SH, SD with that of OH, OD to see the effects of a heavier nucleus on the magnitude of the spin-orbit interaction. In OH the crossing point of the  $A^{2}\Sigma^{+}$  and  $1^{4}\Sigma^{-}$  states occurs between v'=3 and v'=4 and, as a result, the lowest few rotational levels in v'=0 and 1 show no predissociation at all, however, even in v'=3 the lifetime of the highest observed<sup>25,26</sup> rotational level is still as long as 33 ns in contrast with SH (v=1) for which  $\tau < 5$  ps. This is largely a reflection of the smaller spin-orbit coupling matrix elements associated with the first row hydride.

### **VI. CONCLUSIONS**

We have used a combination of experimental and theoretical methods to understand the predissociation of the low vibrational states of SH and SD A  ${}^{2}\Sigma^{+}$ . As is the case with OH, the first electronically excited state of SH is predissociated by three repulsive states, the  $1 \, {}^{4}\Sigma^{-}$ ,  $1 \, {}^{2}\Sigma^{-}$ , and  $1 \, {}^{4}\Pi$ states, which all correlate with  $S({}^{3}P) + H({}^{2}S)$  at large internuclear separation. CRDS measurements of the A-X (1,0) bands of SH and SD and the (2,0) band of SD reveal the rates of predissociation through homogeneous broadening of spectral lines. The lifetimes determined from the predissociation rates have been compared with Fermi Golden Rule calculations that make use of an experimentally derived empirical potential for the  $A^{2}\Sigma^{+}$  state and *ab initio* values for the  $1^{4}\Sigma^{-}$ ,  $1^{2}\Sigma^{-}$ , and  $1^{4}\Pi$  potentials and for the spin-orbit coupling between the bound and repulsive states. The comparison of experimental and theoretical results reveals that the predissociation of the A state levels with  $v' \leq 2$  is dominated by coupling to the 1  ${}^{4}\Sigma^{-}$  state, but that the other repulsive potentials should start to contribute to the predissociation of higher v' levels. The rotational dependence of the predissociation rates determined by us for the v' = 1 level of SH (A) and by others for the v'=0 levels of the A state of SH and SD is reproduced quantitatively by the calculations which show the variation to be the result of centrifugal contributions to the potential energy functions. The value of CRDS as a method of studying fast molecular predissociation is clearly demonstrated.

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