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Fourier-transform-spectroscopic photoabsorption cross sections and oscillator strengths for the S₂ $B^{3}\Sigma_{u}^{-} - X^{3}\Sigma_{q}^{-}$ system

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Photoabsorption cross sections and oscillator strengths for the strong, predissociating vibrational bands, $v \ge 11$, in the S₂ $B^{3}\Sigma_{u}^{-} - X^{3}\Sigma_{g}^{-}(v, 0)$ system are reported. Absorption measurements were undertaken on S₂ vapor produced by a radio-frequency discharge through H₂S seeded in helium, and also in a two-temperature sulfur furnace, at temperatures of 370 K and 823 K, respectively. S₂ column densities were determined in each source by combining experimental line strengths in low-*v* non-predissociating B - X bands (v < 7) with calculated line *f*-values based on measured radiative lifetimes and calculated branching ratios. The broad-band capabilities of two vacuum-ultraviolet Fourier-transform spectrometers, used with instrumental resolutions of 0.22 cm⁻¹ and 0.12 cm⁻¹, respectively, allowed for simultaneous recordings of both non-predissociating and predissociating bands, thus placing the predissociating-band cross sections on a common absolute scale. Uncertainties in the final cross section datasets are estimated to be 15% for the 370-K vapor and 10% for the 823-K vapor. The experimental cross sections are used to inform a detailed predissociation model of the B(v) levels in Paper II [Lewis *et al.*, J. Chem. Phys. **148**, 244303 (2018)]. For astrophysical and other applications, this model can be adjusted simply to provide isotopologue-specific cross sections for a range of relevant temperatures. *Published by AIP Publishing*. https://doi.org/10.1063/1.5029929

I. INTRODUCTION

The ultraviolet absorption spectrum of S₂ is dominated by a progression of bands in the $B^{3}\Sigma_{u}^{-} - X^{3}\Sigma_{g}^{-}$ system. Vibrational bands originating from the lowest vibrational level of the ground state extend from 313 nm to approximately 250 nm. The B - X absorption features, as well as emission bands from the lowest ten vibrational levels of the Bstate, are observed in multiple astrophysical environments. S₂ is recognized as a major constituent of volcanic plumes on Io via absorption in the B - X system;^{1,2} Noll *et al.*³ observed a prominent $S_2 B - X$ absorption signal associated with the impact of comet Shoemaker-Levy 9 on Jupiter; B - X emission from cometary comae has been reported;⁴⁻⁶ and cometary S₂ has been measured via mass spectrometry.^{7,8} Predicted strong $S_2 B - X$ absorption has been invoked by Zahnle *et al.*⁹ as contributing to stratospheric heating in the atmospheres of hot Jupiters. Terrestrially, S₂ is thought to be an important ancient-earth gas-phase species¹⁰ and may play a role in the isotopic fractionation of sulfur in the early earth atmosphere.¹¹ Practical applications of B - X emission include the monitoring of the chemical dynamics of combustion processes^{12,13} and the radiometric properties of sulfur-based discharge lamps.¹⁴ Considerable effort has also gone toward the development of radiative-transfer models for these sulfur discharges.^{15,16}

The B - X system is the S₂ analog of the Schumann-Runge system in the isovalent O_2 molecule and has been the subject of numerous experimental and theoretical studies. In 32 S₂, the v = 0-9 levels of the *B* state lie below the first dissociation limit. The highly perturbed nature of the absorption and emission bands associated with these vibrational levels long hindered the development of a full spectroscopic analysis. Following earlier work by Meakin and Barrow,¹⁷ Meyer and Crosley,¹⁸ Patino and Barrow,¹⁹ Matsumi et al.,²⁰ and Heaven et al.,²¹ Green and Western^{22,23} provided the first comprehensive rotational analysis of the B(0-9) levels. Their analysis was informed by a combination of new rotationally cold laserinduced fluorescence spectra, room temperature fluorescence spectra, and existing high-temperature (~1000 K) absorption spectra from Barrow and co-workers, complemented by new radiative lifetime measurements and those of Matsumi et al.²⁴ As first suggested by Meakin and Barrow,¹⁷ the perturbing state has ${}^{3}\Pi_{u}$ symmetry; it is now labeled as the $B''{}^{3}\Pi_{u}$ state. Green and Western^{22,23} successfully deperturbed the observed spectra by globally fitting the rovibronic levels of B(0-9) and the rovibronic levels of B''(v = 2-21). They presented deperturbed constants for the B and B'' vibrational levels^{22,23} and extracted spin-orbit parameters for the $B \sim B''$ interaction.²²

The B - X(v, v'' = 0) absorption system transitions from sharp rotational structures for $v \le 9$ to highly broadened rotational envelopes for $v \ge 11$, signaling the onset of strong predissociation. Wheeler et al.²⁵ undertook a detailed study of the predissociation mechanisms of the B state. Room temperature band contours were recorded via cavity ring-down spectroscopy for $10 \le v \le 19$. Full-width at half-maximum (FWHM) linewidths, varying from $\Gamma < 1 \text{ cm}^{-1}$ (v = 10) to $\Gamma > 20 \text{ cm}^{-1}$ (v = 19), were extracted or estimated by comparison to spectral simulations of the band profiles. Wheeler et al.²⁵ report a rapid onset of broadening at v = 11, with widths maximizing at 14 cm^{-1} for B(13), followed by gradually decreasing widths, reaching 7 cm⁻¹ for B(17). A second abrupt increase in width occurs at B(18), with the v = 18 and 19 levels having widths estimated by Wheeler et al.²⁵ to be greater than 15 cm⁻¹ and 20 cm⁻¹, respectively. A subsequent velocitymap imaging study of $S({}^{3}P_{J})$ photodissociation products, by Frederix et al.,²⁶ led to a revised value for the lowest dissociation energy and clarification of the relevant dissociation channels for the B(10) and B(11) levels.

Theoretical studies, beginning with the work of Swope *et al.*,²⁷ have provided *ab initio* potential-energy curves for the $B^{3}\Sigma_{u}^{-}$ state (which correlates with the $S(^{3}P) + S(^{1}D)$ dissociation limit) and for the relevant *ungerade* states that correlate with the $S(^{3}P) + S(^{3}P)$ limit. These include the $B''{}^{3}\Pi_{u}$, $1{}^{1}\Pi_{u}$, $1{}^{5}\Pi_{u}$, and $2{}^{3}\Sigma_{u}^{+}$ states. Pradhan and Partridge,²⁸ Kiljunen *et al.*,²⁹ Gai *et al.*,³⁰ and Sarka *et al.*,¹¹ calculated *ab initio* potential-energy curves for the *B* and *B''* states, along with B - X and B'' - X transition-moment functions. Wheeler *et al.*,²⁵ as part of their combined experimental and modeling study, calculated *ab initio* curves for the *B* initio potential curves and evaluate spin-orbit coupling between the *B* state and the *ungerade* states that may contribute to its predissociation.

In this report, we present the first direct measure of the photoabsorption cross sections and oscillator strengths for the strong, predissociating vibrational bands, $v \ge 11$, in the B - X(v, 0) system. The cross sections, recorded at 370 K and 823 K, are used to inform a detailed coupled-channel Schrödinger-equation (CSE) predissociation model of the B(v) levels in Paper II by Lewis *et al.*³³ For astrophysical and other applications, this model can be adjusted simply to provide isotopologue-specific cross sections across the full range of relevant temperatures.

II. EXPERIMENTAL DETAILS

Two complementary sets of photoabsorption measurements were made on S₂ vapor at temperatures of 370 K and 823 K. Both sulfur samples (H₂S precursor gas for the 370 K spectra; solid elemental sulfur for the 823 K spectra) were in natural abundance (32 S 94.93%, 33 S 0.76%, 34 S 4.29%), 34 resulting in S₂ relative abundances of 32 S₂: 32 S³⁴S: 32 S³³S = 1.000:0.090:0.016.

A. Radio-frequency discharge

Measurements were carried out on the high-resolution absorption spectroscopy branch of the DESIRS beamline³⁵ at the SOLEIL synchrotron facility in Saint Aubin, France. The beamline undulator provided a continuum background with an ~7% bandwidth (~2 700 cm⁻¹ FWHM, or 18 nm, at 260 nm). After a gas-filter chamber removed unwanted high harmonics emitted by the undulator source, the continuum light passed through the absorption cell before entering a vacuum-ultraviolet Fourier-transform spectrometer (VUV-FTS).^{36,37} The VUV-FTS is a wave-front division interferometer and relies on a modified Fresnel bi-mirror configuration requiring only flat mirrors. The path difference is scanned through the translation of one reflector. The instrumental resolution was set to 0.86 cm⁻¹ FWHM in the predissociation region and 0.22 cm⁻¹ FWHM in the non-predissociation region.

The 1.5-m glass absorption cell, equipped with wedged MgF2 windows, was outfitted with a radio-frequency discharge apparatus (13.5 MHz, 200 W) at its center. Helium carrier gas, at an upstream pressure ranging from 200 Pa to 400 Pa, flowed through the cell and was continuously pumped via a $600 \text{ m}^3 \text{h}^{-1}$ Roots pump. Hydrogen sulfide (H₂S) was seeded into the He flow prior to the cell at partial pressures of 5 Pa-10 Pa. The rf discharge typically extended about 40 cm on either side of the central discharge cavity. The parent H₂S gas has a weak continuum cross section ($\sim 2 \times 10^{-21}$ cm²) throughout the region of interest,^{38,39} which resulted in a background optical depth of 0.02-0.03. With the discharge on, strong S₂ features were observed; $S_2 B - X$ optical depths in the strongest predissociated bands were typically ~ 0.8 , with optical depths in the non-predissociating bands reaching ~ 2-3. Figure 1 displays the transmission signal resulting from 10 co-added scans in one undulator bandpass. No spectral features from species other than S₂ (and the H₂S precursor gas) were observed. Four overlapping undulator bandpasses were needed to span the 33 500–41 500 cm^{-1} region. A sequence of five scans was recorded for each bandpass: pure He with no discharge; He plus H_2S with no discharge; He plus H_2S in a 200 W discharge, and then a repeat of the two nodischarge scans. The same sequence of scans, with identical pressure and power settings, was carried out for each undulator window. The signal-to-noise ratio at the peak



FIG. 1. Transmittance spectrum for flowing rf discharge of H₂S seeded in helium, showing a portion of the S₂ B - X(v, 0) progression. Upper curve (red): no discharge. Lower curve (black): discharge on. The first strongly predissociated feature, at ~36 100 cm⁻¹, is the (11, 0) band.

of each undulator bandpass (for 10 co-added scans) was typically ~100.

The optical depths of S₂ features were determined for each undulator spectral window using the He plus H₂S (no discharge) background scans to define the continuum level. A small, but undetermined, fraction of the precursor H₂S gas was dissociated in the rf discharge, leading to some uncertainty in the true value of the continuum. However, as the H₂S absorption signal, in the absence of the discharge, ranged from 2% to 3%, the resulting uncertainty in the continuum level is minimal. Optical depths from the four overlapping undulator windows were combined to produce a composite optical depth dataset spanning the 33 500-41 000 cm⁻¹ region; the dataset is displayed in Fig. 2. The S₂ temperature in the discharge source was determined to be 370 K, with an estimated uncertainty of ~ 10 K,⁴⁰ from measurements of rotational line strengths in the non-predissociated bands (Sec. III A) and modeling of the rotational structure in the predissociated bands (the details of the modeling procedure are presented in Paper II^{33}). The relative strengths of B - X(v, 1) hot bands in the predissociation region are consistent with the assignment of a single S₂ temperature.³³

Weak, sharp structure, originating from the S₂ metastable $a^{1}\Delta_{g}$ state, was observed in the 38 800–40 850 cm⁻¹ region. The features are associated with six vibrational bands, $f^{1}\Delta_{u}(5-10) - a^{1}\Delta_{g}(0)$.⁴¹ No analysis of these features was undertaken in the present study.

B. Two-temperature furnace

Absorption spectra of S_2 vapor in a two-temperature furnace were recorded with the vacuum ultraviolet FTS^{42,43} at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. An absorbing column of S_2 vapor was produced from heated elemental sulfur. The optimum conditions for generating S_2 in the absence of other sulfur allotropes (S_3 through S_8) require a combination of high temperature and low pressure (relative to the equilibrium vapor pressure at that



FIG. 2. Optical depth of $S_2 B - X$ features in H_2S rf discharge at an estimated temperature of 370 K, constructed from a composite of four overlapping spectral windows and recorded at a resolution of 0.22 cm⁻¹ FWHM. Vibrational bands in the (v, 0) progression can be followed to v = 27.

temperature).⁴⁴ These conditions were established using a lowtemperature (390–490 K) side-arm reservoir of sulfur and a high-temperature (823 K) absorption path. A 2.54-cm diameter and 2.5-cm long quartz cell, encased in a heated 10-cm long stainless steel conduction block, defined the absorption path. The conduction block, in thermal contact with the absorption cell, was heated by two 400-W band heaters and its temperature monitored with two thermocouples. Temperature control was not used for the high-temperature cell; due to the large thermal mass of the conduction block, the temperature of the assembly remained constant within ±5 K. The sulfur reservoir, located at the end of a 10.2-cm long quartz sidearm, sat in a heated copper conduction block. A home-built proportional-integral control temperature controller maintained the reservoir temperature to better than ±0.2 K.

Absorption spectra were recorded at a resolution of 0.10 cm⁻¹ FWHM over a range of sulfur reservoir temperatures (and, hence, sulfur column densities at 823 K). A 1000-W xenon arc lamp was used as a continuum light source. The NIST FTS has dual output channels; with appropriate optical filters and detectors, the two channels were used to monitor absorption in two spectral windows. The 31 000–43 000 cm⁻¹ region, which includes all of the B - X bands of interest in our study, was recorded with a solar-blind photomultiplier tube and a UG5 bandpass filter. The 23 000-40 000 cm⁻¹ region was monitored simultaneously with another photomultiplier and UG5 filter. The second spectral window provided an enhanced signal-to-noise ratio for the low-v B - X vibrational bands and it allowed for the monitoring of possible S₃ absorption features, which were reported to peak at $25\,000\,\text{cm}^{-1}$ by Billmers and Smith.45

Spectra were recorded for seven S₂ column densities, corresponding to sulfur reservoir temperatures ranging from 393 to 488 K. Based on the known temperature dependence of the equilibrium vapor pressure over elemental liquid sulfur,⁴⁶ total cell pressures are estimated to range from 3 Pa to ~300 Pa. As pointed out by Meyer⁴⁴ and Eckert and Steudel,⁴⁷ the concentration of S₂ relative to the larger allotropes increases dramatically in conditions of high temperature and low pressure. While the exact distribution of sulfur allotrope concentrations in the unsaturated vapor of the absorption cell is unknown, Meyer⁴⁴ reports that at 1000 K and 130 Pa, S₂ constitutes ~99% of the gas composition.

For each column density, continua with signal-to-noise ratios of ~100 were achieved by co-adding up to 100 interferograms, each of approximately 60 s, giving a total integration time for each column density of about 1.5 h. Because of the excessive times required to heat and cool the reservoir and the absorption cell, it was not feasible to record empty-cell transmission spectra before and after each absorption run. Instead, empty-cell spectra were recorded twice per day, once before the reservoir was heated and once at the conclusion of the day when the reservoir had sufficiently cooled to remove the S_2 vapor from the cell. Modest variations in the continua intensities were observed in the pairs of empty-cell spectra, likely due to sulfur deposition on the cell windows. In the initial processing of the data, the continua were defined for each absorption run by scaling the empty-cell scans so as to match the transmittance spectra in the regions of zero S_2 absorption.



FIG. 3. Transmittance spectra of S_2 vapor generated in a two-temperature furnace; the temperature of the absorbing column is 823 K. Lower curves: 31 000–43 000-cm⁻¹ channel. Upper curves: 23 000–40 000-cm⁻¹ channel. Red: Xe-lamp continua. Black: Transmitted signal, showing $S_2 B - X$ features. No absorption is seen below the B - X bands, verifying the absence of significant columns of either S_3 or S_4 .

Figure 3 displays the continua and transmittance spectra recorded by the two channels of the FTS for a sulfur reservoir temperature of 450 K after the initial scaling procedure was applied. Because of the absence of continuum absorption in the longer-wavelength channel, the scaling procedure for that channel was more reliable than that for the shorter-wavelength channel. Any inconsistencies in the deduced optical depths in the region of spectral overlap were then minimized by further adjustments to the shorter-wavelength channel continuum.

No spectral features associated with S_3 or larger allotropes were observed in the longer-wavelength channel. Modeling of the predissociation region,³³ based on the cross sections generated in this report, reveals a weak continuum absorption contribution, possibly associated with S_8 ,^{48,49} spanning the 35 700–38 500 cm⁻¹ region.

III. PHOTOABSORPTION CROSS SECTIONS

The measured S_2 optical depths $\delta(v)$ in our absorption spectra can be converted to photoabsorption cross sections $\sigma(v)$, given a knowledge of the S_2 column densities N, using the relation $\sigma(v) = \delta(v)/N$. However, there is no direct measure of the S_2 column density in either the flowing H₂S discharge or the two-temperature S_2 furnace, and therefore, it is necessary to find an independent method for column-density and cross section calibration.

A. Column-density calibration

Our measurements are placed on an absolute scale by (i) using known radiative lifetimes of the low-lying (and nonpredissociating) *B*-state vibrational levels, together with calculated emission branching ratios for B - X(v, v''), to determine B - X(v, 0) band *f*-values and (ii) using those band *f*-values with our measured line strengths in the non-predissociating bands to establish the S₂ column density. Taking advantage of the broad-band capabilities of the FT spectrometers, which measure the entire B - X absorption band system simultaneously, we can then place the predissociating band cross sections on an absolute scale. The details of this procedure are outlined below.

Radiative lifetimes of the non-predissociating $B(v \le 8)$ levels were measured by Quick and Weston,⁵⁰ Matsumi et al.,²⁴ and Green and Western.²² Quick and Weston⁵⁰ recorded fluorescence lifetimes ranging from 30 to 45 ns from relatively broadband (0.5 cm⁻¹ FWHM) excitation of bandheads in an 873-K furnace. Under these conditions, many upper rotational levels will be accessed simultaneously. Matsumi et al.²⁴ excited single rotational lines in a supersonic expansion and found lifetimes ranging from 34 ns to 48 ns. The mixing of the $B^{3}\Sigma_{\mu}^{-}$ and $B^{\prime\prime}{}^{3}\Pi_{\mu}$ states strongly affects the radiative lifetimes of individual rotational levels. The small B'' - X transition moment^{28,29} results in a corresponding "pure" B"-state radiative lifetime of ~6 μ s.²⁹ Strongly mixed rotational levels will therefore have lifetimes that are significantly longer than those of pure B-state character. Green and Western,²² in their deperturbation study of the *B* and B'' states, quantified the extent of the $B \sim B''$ mixing and examined the measured radiative lifetimes of Matsumi et al.²⁴ as a function of the percentage of B-state character. Their extrapolation of the lifetime to 100% B-state character yielded a pure B-state lifetime of 32 ± 1 ns (see Fig. 11 of Ref. 22). In this work, we adopt the Green and Western²² B-state lifetime value of 32 ns and use it to calculate the B - X(v, 0) absorption oscillator strengths, as described in the following paragraphs.

The only electric-dipole-allowed radiative transitions from a B(v) level are to the vibrational levels of the ground state, X(v''). Therefore, in the absence of collisions, the corresponding radiative lifetime is given by

$$\tau_{v} = 1 / \sum_{v''} A_{v,v''},$$
 (1)

where the $A_{v,v''}$ are Einstein-*A* coefficients for the B - X(v, v'') transitions, and $A_{v,v''} \propto \gamma_{v,v''}^3 \mu_{v,v''}^2$, where $v_{v,v''}$ is the transition wavenumber and $\mu_{v,v''}$ is the corresponding electricdipole transition matrix element.⁵¹ Thus, each term in the sum of Einstein-*A* coefficients can be expressed in terms of $A_{v,0}$, according to

$$A_{v,v''} = A_{v,0} \left(\frac{\nu_{v,v''}}{\nu_{v,0}}\right)^3 \left(\frac{\mu_{v,v''}}{\mu_{v,0}}\right)^2.$$
 (2)

From Eqs. (1) and (2), we have

$$A_{v,0} = \frac{\nu_{v,0}^{3} \mu_{v,0}^{2}}{\tau_{v} \sum_{v''} \nu_{v,v''}^{3} \mu_{v,v''}^{2}}.$$
(3)

Finally, each B - X(v, 0) band oscillator strength is given by $f_{v,0} = 1.50A_{v,0}/v_{v,0}^2$,⁵¹ where v is in cm⁻¹.

The relevant dipole matrix elements and transition energies were calculated from X-state and B-state potential-energy curves and the B - X electronic transition moment. The B-state potential-energy curve (PEC) of Lewis *et al.*,³³ optimized in a CSE model to reproduce line positions and widths throughout the B - X system, was adopted for the present calculations. A ground-state Rydberg-Klein-Rees PEC was constructed from the spectroscopic constants of Green and Western²² for v'' = 0-7, supplemented by $v'' \le 32$ vibrational energies⁵² and rotational constants.^{53,54} The *ab initio* B - X electronic transition moment of Pradhan and Partridge²⁸ was also adopted.

Our calculated pure B - X(v, 0) band oscillator strengths for $2 \le v \le 6$, following normalization to the 32-ns lifetime of Ref. 22 by scaling the electronic transition moment of Ref. 28, along with those computed by Pradhan and Partridge,²⁸ are listed in Table I. While predissociation is not present in any of the B(v < 10) levels, mixing of the B and B'' states is very strong in the B(7-9) levels, precluding their use as experimental column-density calibrators. The *f*-values listed in Table I are, strictly speaking, only valid for J = 0: we refer to them as rotationless band *f*-values.⁵⁵ The large discrepancies between our calculated *f*-values and those of Pradhan and Partridge²⁸ have two origins. The most significant difference in the calculations stems from the chosen PECs. For the purpose of their *f*-value calculation, Pradhan and Partridge²⁸ constructed analytic PECs of the type developed by Murrell and Sorbie,⁵⁶ based on the experimental spectroscopic constants tabulated by Huber and Herzberg.⁵⁷ Their resulting *B*-state PEC differs significantly from the CSE-optimized PEC of Lewis et al.³³ which is used here, and this difference is the primary source of the *f*-value discrepancy.⁵⁸ A secondary contribution comes from our scaling of the Pradhan and Partridge²⁸ electronic transition moment. When combined with the PECs of Lewis et al.,³³ the electronic transition moment of Ref. 28 produces radiative lifetimes of ~37 ns for $B(v \le 7)$. Agreement with the measured pure lifetime of 32 ns,²² adopted in this work, requires scaling the square of the electronic transition moment of Ref. 28 by a factor of ~1.15. As a consistency check, we were able to reproduce the tabulated f-values of Pradhan and Partridge²⁸ using their analytic PECs and unscaled electronic transition moment.

Our calculated rotationless band *f*-values were combined with measurements of individual line strengths in multiple low-v B - X(v, 0) bands to determine column densities in the two S₂ datasets. For the 823-K spectra, 10 to 40 lines were analyzed in each of the (2–6, 0) bands, with *J* values ranging from ~10 to ~60. In the data reduction, the transmitted intensity I(v) is related to the *measured* optical depth $\delta_{exp}(v)$, which includes the effects of the finite instrumental resolution, through application of the Beer-Lambert law, $I(v) = I_0(v) \exp[-\delta_{exp}(v)]$, where $I_0(v)$ is the source background continuum level. For each fitted line within a band, a leastsquares fitting routine that accounts for the effect of the finite instrumental resolution was used to determine a value for

TABLE I. Rotationless pure B - X(v, 0) band *f*-values for five low-*v* bands.

v	$f_{v,0} \times 10^{4a}$	$f_{v,0} \times 10^{4t}$
2	1.39	0.5
3	4.12	1.5
4	9.54	3.3
5	18.5	6.3
6	30.8	10.6

^aPresent work.

the line's corrected integrated optical depth. All rotational lines were modeled with Gaussian profiles determined by an appropriate Doppler width (0.060 cm⁻¹ FWHM at 370 K and 0.090 cm⁻¹ FWHM at 823 K). The instrument functions were described by sinc functions reflecting the instrumental resolutions, which result from the finite path differences in the recorded interferograms (0.22 cm⁻¹ FWHM for the SOLEIL VUV-FTS and 0.12 cm⁻¹ FWHM for the NIST FTS).

By varying the position and integrated optical depth for each line, the least-squares fitting routine minimized the difference between a model transmission spectrum (calculated by a convolution of the line's Gaussian profile in absorption with the instrumental sinc function) and the measured transmission spectrum. Fitting uncertainties in the integrated optical depths were assessed by the least-squares routine: they varied according to the signal-to-noise ratio of each spectrum and the strength of the absorption and were typically ~3%.

The integrated optical depths of individual rotational lines, determined from the fitting procedure, were converted into products of line oscillator strengths, $f_{J,J''}$, and S₂ X(0) column densities according to⁵⁹

$$Nf_{J,J''} = 1.13 \times 10^{12} \left(\frac{\int \delta(\nu) d\nu}{\alpha_{J''}} \right),$$
 (4)

where the integrated optical depth is in units of cm⁻¹ and $\alpha_{J''}$ is the fractional population of S₂ molecules in the v'' = 0, J'' rotational level, as determined from a normalized Boltzmann factor based on S₂ ground-state term values calculated from the constants of Fink⁶⁰ and the ${}^{3}\Sigma_{g}^{-}$ Hamiltonian of Amiot and Verges.⁶¹

For transitions to unperturbed upper vibronic states, band f-values are related to rotational line f-values by Hönl-London factors. Tatum and Watson⁶² formulated Hönl-London factors for ${}^{3}\Sigma^{\pm} - {}^{3}\Sigma^{\pm}$ transitions for states with coupling intermediate between Hund's cases (a) and (b). To avoid uncertainties associated with the extent of the coupling in the B state, only transitions in the P_2 and R_2 branches were used for column density calibration purposes.⁵⁵ Individual line strengths are affected by the extent of $B \sim B''$ mixing which, within each band, is strongly dependent on J. Mixing coefficients, based on the deperturbation analysis of Green and Western²² (provided to the authors by Western⁶³), were used as additional correction factors in the data reduction, in order to determine deperturbed line strengths. Whenever possible, lines were chosen that terminate on upper-state vibronic levels with correction factors <10%.

As is well known, for diatomic molecules in which the ground- and excited-state PECs differ significantly, the corresponding effective band oscillator strengths can vary systematically with rotation, due to the differential effects of the centrifugal-energy term on each potential. For example, in the case of the analogous B - X Schumann-Runge system of the isovalent molecule O₂, the effective band oscillator strengths are known to decrease with increasing rotation.⁶⁴ The same effect was observed for the S₂ discrete bands studied here: for each band, $Nf_{v,0}(J, J'')$ decreases approximately linearly with J(J + 1). For one high-temperature (823 K) absorption spectrum, Fig. 4 shows the derived products of deperturbed



FIG. 4. Products of ${}^{32}S_2 X(0)$ absorbing column density and B - X deperturbed, effective band *f*-values for five bands (2–6, 0) as a function of J(J + 1). The rotational dependences of *Nf* are due to the differential centrifugal effects (see the text). The unknown S₂ column density is determined by combining linear extrapolations of *Nf* to J = 0 with calculations of the rotationless band *f*-values (see the text and Table II).

band *f*-values and ${}^{32}S_2 X(0)$ column density $(Nf_{n,0})$ for the B - X(2 - 6, 0) bands, determined from individual line strength measurements. A linear extrapolation to J = 0 determines the product of the rotationless band *f*-value and column density. Table II lists the $Nf_{v,0}$ values and the column density determined from each band, where the $f_{v,0}$ values are taken from Table I. The weighted average of the X(0) column densities is $4.20(11) \times 10^{16}$ cm⁻². Taking into account the relative vibrational populations of the X(0-3) levels at 823 K, the total ${}^{32}S_2$ column density is 5.88(15) × 10¹⁶ cm⁻², corresponding to a ³²S₂ partial pressure in the absorption cell of 250 Pa. The same column-density calibration procedure was followed for the 370-K absorption spectrum recorded in the H₂S discharge. Only one low-v vibrational band, B - X(5, 0), was used for the calibration because of strongly saturated lines in B - X(6, 0) and the limits of the undulator bandpass. Sixteen rotational lines were measured, with J < 40, yielding a 32 S₂ X(0) column density of 1.26(10) × 10¹⁶ cm⁻² and a total 32 S₂ column density of 1.34(11) × 10¹⁶ cm⁻².

The uncertainties in the deduced column densities described above, 8% for the 370-K dataset and 3% for the 823-K dataset, are statistical, resulting from the determination of the products of rotationless band f-values and column densities from individual rotational line strengths. Additional sources of uncertainty must be included in an estimation of total uncertainties for the S₂ photoabsorption cross sections.

TABLE II. ${}^{32}S_2 X(0)$ column densities for 823 K scan.^a

Band	Nf (cm ⁻²)	<i>N</i> (cm ⁻²)
$\overline{B - X(2, 0)}$	5.72(46) × 10 ¹²	$4.12(33) \times 10^{16}$
B - X(3, 0)	$1.92(9) \times 10^{13}$	$4.66(22) \times 10^{16}$
B - X(4, 0)	$4.15(11) \times 10^{13}$	$4.35(11) \times 10^{16}$
B - X(5, 0)	$7.43(21) \times 10^{13}$	$4.02(11) \times 10^{16}$
B - X(6, 0)	$1.26(5) \times 10^{14}$	$4.09(13) \times 10^{16}$
Weighted average		$4.20(11) \times 10^{16}$

^aUncertainties, in units of the least-significant figure, are given in parentheses

There are two sources of uncertainty in the conversion of measured radiative lifetimes to band f-values for the low-vbands: (i) Green and Western²² estimate the uncertainty in the measured pure B lifetime of 32 ns to be ± 1 ns; (ii) branching ratios for the B - X(v, v'') transitions rely on choices of upper and lower state wave functions and the shape of the transition-moment function. Confidence in the chosen PECs and transition-moment function stems from the success in the detailed modeling of the two photoabsorption datasets;³³ we estimate branching-ratio uncertainties to be on the order of a few percent. The S₂ temperatures, 370 K and 823 K, are estimated to have uncertainties of ~10 K; these uncertainties affect, at a few percent level, the calculated rotational populations, and, hence, the derived J-dependence of band f-values. Finally, there is the possibility of contaminants in the gas samples. The isotopic abundances of ³²S and ³⁴S in the precursor materials result in a ${}^{32}S^{34}S$ population that is 9.0% that of ${}^{32}S_2$. The ³²S³⁴S spectrum is fully accounted for in the photoabsorption model, so its contributions to the measured cross sections are well understood. Other contaminants might include larger sulfur allotropes. Given these multiple contributions, not all of which are easily quantified, we estimate final fractional uncertainties in the column densities of our samples to be $\sim 15\%$ for the 370-K spectrum and ~10% for the 823-K spectrum; these uncertainties translate into identical uncertainties in our derived cross sections.

B. Cross sections

Figure 5 displays our final photoabsorption cross sections at 370 K and 823 K for the $B - X(v \ge 10, 0)$ bands. The onset of strong predissociation is evident for $v \ge 11$. Lines in the (10, 0) band display moderate broadening; only Doppler and instrumental broadening is seen in the lower-v bands. At



FIG. 5. Photoabsorption cross sections of the predissociation region of the $S_2 B - X$ system at 370 K and 823 K. For clarity, the 823-K cross section is offset by 1×10^{-16} cm². The locations of the (v, 0) bands with $v \ge 11$ and the (v, 1) hot bands with $v \ge 13$ are indicated [upper (blue) and lower (red) vertical tick marks, respectively]. Hot bands are visible in both spectra, particularly above 38 000 cm⁻¹, but are much more prominent in the 823-K spectrum. The large differences in peak cross sections between the two datasets are due only to the effects of temperature on the rotational envelopes. Weak, sharp features seen in the 370-K spectrum above 39 500 cm⁻¹ are bands from the $f^{-1}\Delta_u - a^{-1}\Delta_g$ system of metastable S₂ produced in the rf discharge.

both temperatures, there is significant population in the X(1)level, and (v, 1) hot bands are clearly seen above 38 000 cm⁻¹ in both spectra shown in Fig. 5, but much more in the 823-K spectrum, where (v, 2) hot bands are also a minor factor. B - X bands due to absorption by the ${}^{32}S^{34}S$ isotopologue also occur in each spectrum at the at the $\sim 9\%$ level, producing small inflections in the low-energy wings for each band of the normal isotopologue, but these are difficult to discern in the experimental cross sections of Fig. 5 without further analysis. The striking difference in peak cross sections between the two spectra is due entirely to the temperature difference and the corresponding relative rotational-population differences. CSE modeling of the cross sections, performed in the companion work,³³ indicates small continuum contributions to the measured cross sections (at a level of $\sim 2-3 \times 10^{-18} \text{ cm}^2$) that are not due to absorption from the $S_2 X$ state. Discounting these weak continuum features, the integrated cross sections of the two datasets are consistent at approximately the 10% level, well within the estimated relative uncertainties of the cross sections.

C. Oscillator strengths

The calibrated cross sections of Fig. 5 enable the determination of experimental B - X(v, 0) photoabsorption oscillator strengths, through the fitting of appropriate band models, although this process is complicated by band overlap, hot bands, isotopic contamination, and underlying continua. These problems can be managed by using the CSE model, described in detail in Ref. 33, which is shown to be able to accurately reproduce the shapes of individual band envelopes in the predissociation region and scaling its intensity individually for each band. The rotationless experimental oscillator strengths determined in this way for $v \ge 11$ from both the 370-K and 823-K cross sections are shown in Fig. 6 (open



FIG. 6. Rotationless band oscillator strengths for the B - X(v, 0) system of ${}^{32}S_2$. Solid curve (blue): Deperturbed computed *f*-values, scaled to be consistent with the experimental lifetime of 32 ns, as described in Sec. III A. Open circles (red): Experimental *f*-values deduced from the 370-K cross section of Fig. 5 by fitting the CSE model of Ref. 33 separately to each band profile. Solid circles (black): Experimental *f*-values deduced from the 823-K cross section of Fig. 5. For the predissociated region, $v \ge 11$, the 823-K *f*-values were determined similarly to the 370-K values, but those for the discrete (2–6, 0) bands are deperturbed experimental *f*-values, determined from Table II using the weighted-average calibrated column density.

red circles and filled black circles, respectively). We note that these *f*-values result essentially from matching the areas of the experimental and model band cross sections and are dependent on the model parameters only in the second order, through the implicit corrections for band overlap, hot bands and isotopic bands, the underlying continuum being essentially a free parameter.⁶⁵ The statistical uncertainties in the corresponding relative experimental oscillator strengths vary from 2-3% for the strongest bands to $\sim 30\%$ for the weakest bands analyzed [(24, 0) for T = 823 K, (27, 0) for T = 370 K], and there isexcellent agreement between the relative results for the two temperatures within these combined uncertainties. The small systematic difference between the two datasets, with the 370-K f-values higher, is simply a reflection of the non-negligible calibration uncertainties for the corresponding column densities, as described in Sec. III A.

For completeness, the experimental rotationless oscillator strengths for the discrete (2–6, 0) bands, deduced from the 823-K spectrum, are also included in Fig. 6. These *f*-values follow from the J = 0 intercepts of Fig. 4, the corresponding *Nf* values listed in Table II, and the adopted weighted-average for the corresponding column density. They are depertubed values, the intensity effects of the $B \sim B''$ interaction having been removed using the mixing factors of Green and Western,^{22,63} as described in Sec. III A.⁶⁶

Finally, the solid curve (blue) in Fig. 6 shows the full deperturbed rotationless oscillator-strength distribution, computed as in Sec. III A and consistent with the (2–6, 0) *f*-values given in Table I. This was a single-channel calculation employing the diabatic B_1 - and X-state potential-energy curves of Ref. 33, together with the electronic transition moment of Pradhan and Partridge,²⁸ scaled up so as to be consistent with the 32-ns pure *B*-state lifetime of Green and Western.²² There is excellent agreement between the 823-K experimental and computed relative oscillator-strength distributions in Fig. 6, each peaking at v = 12. The difference of ~4% between the peak *f*-values is acceptably small, considering the uncertainties inherent in the column-density-calibration and experimental fitting procedures.

IV. CONCLUSIONS

Our S₂ B - X cross sections provide the first experimental measure of band oscillator strength in the region above the first dissociation limit, where the B - X absorption features are most prominent. In combination with the accompanying coupled Schrödinger-equation predissociation model,³³ they can be used to calculate isotopologue-specific cross sections across a full range of temperatures relevant to astrophysical and other applications.

The room-temperature photoabsorption cross sections calculated recently by Sarka *et al.*¹¹ (see Fig. 3 of Ref. 11), indicating peak cross sections of ~ 1.1×10^{-15} cm², do not account for the highly broadened lines in the predissociating bands, and thus are extreme overestimates of the true peak cross sections. The isotopic fractionation effects associated with the B - X absorption system, as discussed by Sarka *et al.*,¹¹ will be strongly influenced by line broadening and likely need to be revisited.

SUPPLEMENTARY MATERIAL

See supplementary material for tabulations of the calibrated cross-sectional data presented in Fig. 5.

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- ¹J. R. Spencer, K. L. Jessup, M. A. McGrath, G. E. Ballester, and R. V. Yelle, Science **288**, 1208 (2000).
- ²K. L. Jessup, J. R. Spencer, and R. V. Yelle, Icarus **192**, 24 (2007).
- ³K. S. Noll, M. A. McGrath, L. M. Trafton, S. K. Atreya, J. J. Caldwell, H. A. Weaver, R. V. Yelle, C. Barnet, and S. Edgington, Science 267, 1307 (1995).
- ⁴M. F. A'Hearn, P. D. Feldman, and D. G. Schleicher, Astrophys. J. **274**, L99 (1983).
- ⁵P. D. Feldman, H. A. Weaver, M. F. A'Hearn, M. C. Festou, J. B. McPhate, and G.-P. Tozzi, Bull. Am. Astron. Soc. **31**, 1127 (1999).
- ⁶S. J. Kim, M. F. A'Hearn, D. D. Wellnitz, R. Meier, and Y. S. Lee, *Icarus* 166, 157 (2003).
- ⁷L. Le Roy *et al.*, Astron. Astrophys. **583**, A1 (2015).
- ⁸U. Calmonte *et al.*, Mon. Not. R. Astron. Soc. **462**, S253 (2016).
- ⁹K. Zahnle, M. S. Marley, R. S. Freedman, K. Lodders, and J. J. Fortney, Astrophys. J. **701**, L20 (2009).
- ¹⁰A. A. Pavlov and J. F. Kasting, Astrobiology 2, 27 (2002).
- ¹¹K. Sarka, S. O. Danielache, A. Kondorskiy, and S. Nanbu, Chem. Phys. 488, 36 (2017).
- ¹²B. Mischler, P. Beaud, T. Gerber, A. P. Tzannis, and P. P. Radi, Combust. Sci. Technol. **119**, 375 (1996).
- ¹³P. P. Radi, B. Mischler, A. Schlegel, A. P. Tzannis, P. Beaud, and T. Gerber, Combust. Flame **118**, 301 (1999).
- ¹⁴N. D. Gibson and J. E. Lawler, J. Appl. Phys. 79, 86 (1996).
- ¹⁵H. van der Heijden, J. van der Mullen, J. Baier, and A. Körber, J. Phys. B: At., Mol. Opt. Phys. **35**, 3633 (2002).
- ¹⁶C. W. Johnston, H. W. P. van der Heijden, A. Hartgers, K. Garloft, J. van Dijk, and J. J. A. M. van der Mullen, J. Phys. D: Appl. Phys. **37**, 211 (2004).
- ¹⁷J. E. Meakin and R. F. Barrow, Can. J. Phys. 40, 377 (1962).
- ¹⁸K. A. Meyer and D. R. Crosley, Can. J. Phys. **51**, 2119 (1973).
- ¹⁹P. Patiño and R. F. Barrow, J. Chem. Soc., Faraday Trans. 78, 1271 (1982).
- ²⁰Y. Matsumi, T. Munakata, and T. Kasuya, J. Chem. Phys. **81**, 1108 (1984).
- ²¹M. Heaven, T. A. Miller, and V. E. Bondybey, J. Chem. Phys. **80**, 51 (1984).
- ²²M. E. Green and C. M. Western, J. Chem. Phys. **104**, 848 (1996).
- ²³M. E. Green and C. M. Western, J. Chem. Soc., Faraday Trans. **93**, 365 (1997).
- ²⁴Y. Matsumi, T. Suzuki, T. Munakata, and T. Kasuya, J. Chem. Phys. 83, 3798 (1985).
- ²⁵M. D. Wheeler, S. M. Newman, and A. J. Orr-Ewing, J. Chem. Phys. 108, 6594 (1998).
- ²⁶P. W. J. M. Frederix, C.-H. Yang, G. C. Groenenboom, D. H. Parker, K. Alnama, C. M. Western, and A. J. Orr-Ewing, J. Phys. Chem. A **113**, 14995 (2009).
- ²⁷W. C. Swope, Y.-P. Lee, and H. F. Schaefer, J. Chem. Phys. **70**, 947 (1979).
- ²⁸A. D. Pradhan and H. Partridge, Chem. Phys. Lett. **255**, 163 (1996).
- ²⁹T. Kiljunen, J. Eloranta, H. Kunttu, L. Khriachtchev, M. Pettersson, and M. Rasanen, J. Chem. Phys. **112**, 7475 (2000).
- ³⁰Z. Gai, B. Yan, X. Yu, R. Li, J. Yu, S. Pan, and D. Chen, J. Russ. Laser Res. 32, 99 (2011).
- ³¹B. Yan, S.-F. Pan, Z. G. Wang, and J.-H. Yu, Acta Phys. Sin. 54, 5618 (2005).
- ³²W. Xing, D. Shi, J. Sun, H. Liu, and Z. Zhu, Mol. Phys. 111, 673 (2013).

- ³³B. R. Lewis, S. T. Gibson, G. Stark, and A. N. Heays, J. Chem. Phys. 148, 244303 (2018).
- ³⁴K. J. R. Rosman and P. D. P. Taylor, Pure Appl. Chem. **71**, 1593 (1999).
- ³⁵DESIRS: Dichroïsme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron, L. Nahon, N. de Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde, and F. Polack, J. Synchrotron Radiat. **19**, 508 (2012).
- ³⁶N. de Oliveira, M. Roudjane, D. Joyeux, D. Phalippou, J. C. Rodier, and L. Nahon, Nat. Photonics 5, 149 (2011).
- ³⁷N. de Oliveira, D. Joyeux, M. Roudjane, J.-F. Gil, B. Pilette, L. Archer, K. Ito, and L. Nahon, J. Synchrotron Radiat. 23, 887 (2016).
- ³⁸C. Y. R. Wu and F. Z. Chen, J. Quant. Spectrosc. Radiat. Transfer 60, 17 (1998).
- ³⁹H. Grosch, A. Fateev, and S. Clausen, J. Quant. Spectrosc. Radiat. Transfer 154, 28 (2015).
- 40 All uncertainties given herein are 1σ .
- ⁴¹M. Carleer and R. Colin, J. Phys. B: At. Mol. Phys. 3, 1715 (1970).
- ⁴²A. P. Thorne, C. J. Harris, I. Wynne-Jones, R. C. M. Learner, and G. Cox, J. Phys. E: Sci. Instrum. **20**, 54 (1987).
- ⁴³U. Griesmann, R. Kling, J. H. Burnett, and L. Bratasz, Proc. SPIE 3818, 180 (1999).
- ⁴⁴B. Meyer, Chem. Rev. 76, 367 (1976).
- ⁴⁵R. I. Billmers and A. L. Smith, J. Phys. Chem. **95**, 4242 (1991).
- ⁴⁶D.-Y. Peng and J. Zhao, J. Chem. Thermodyn. **33**, 1121 (2001).
- ⁴⁷B. Eckert and R. Steudel, Top. Curr. Chem. **231**, 31 (2003).
- ⁴⁸A. M. Bass, J. Chem. Phys. 21, 80 (1953).
- ⁴⁹T. V. Oommen, Ph.D. thesis, University of Michigan, 1970.
- ⁵⁰C. R. Quick and R. E. Weston, J. Chem. Phys. 74, 4951 (1981).
- ⁵¹H. Lefebvre-Brion and R. W. Field, *The Spectra and Dynamics of Diatomic Molecules* (Elsevier, San Diego, 2004), pp. 348–350.
- ⁵²D. A. Peterson and L. A. Schlie, J. Chem. Phys. **73**, 1551 (1980).
- ⁵³J. M. Ricks, Ph.D. thesis, University of Oxford, 1970.
- ⁵⁴A. L. Smith and J. B. Hopkins, J. Chem. Phys. 75, 2080 (1981).
- ⁵⁵Herein, we employ the rotational quantum number *J*, rather than *N*, since we are considering only F_2 triplet sublevels, for which J = N. This Hund's case-(a) labeling is appropriate for comparison with theoretical calculations. In the case of the $B^{3}\Sigma_{u1}^{-}$ state, $J = 1, 3, 5, \ldots$ and thus the convenient extrapolation to J = 0 is to a virtual level.
- ⁵⁶J. N. Murrell and K. S. Sorbie, J. Chem. Soc., Faraday Trans. 70, 1552 (1974).
- ⁵⁷K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), p. 564.
- ⁵⁸The B-state potential-energy curve of Ref. 33 is spectroscopically accurate up to v = 27 and produces correctly the experimental B X intensity profile, with a maximum near the (12, 0) band, while the polynomial curve of Ref. 28 results in a maximum near the (15, 0) band, in significant disagreement.
- ⁵⁹D. C. Morton and L. Noreau, Astrophys. J., Suppl. Ser. **95**, 301 (1994).
- ⁶⁰E. H. Fink, H. Kruse, and D. A. Ramsay, J. Mol. Spectrosc. **119**, 377 (1986).
- ⁶¹C. Amiot and J. Verges, Can. J. Phys. 59, 1391 (1981).
- ⁶²J. B. Tatum and J. K. G. Watson, Can. J. Phys. 49, 2693 (1971).
- ⁶³C. M. Western, private communication (December 13, 2013).
- ⁶⁴B. R. Lewis, L. Berzins, and J. H. Carver, J. Quant. Spectrosc. Radiat. Transfer **36**, 209 (1986).
- ⁶⁵The overall isotopic contribution to the cross section is ~10%. At T = 823 K, the overall hot-band contribution is ~40%, while the band overlap is $\leq 15\%$. At T = 370 K, the hot-band contribution decreases to ~7% and the band overlap is negligible. The estimated uncertainty introduced into the experimental oscillator strengths due to these factors is $\leq 3\%$ at 370 K and $\leq 5\%$ at 823 K.
- ⁶⁶The intensity effects on the rotationless oscillator strengths for the B X(v, 0) discrete bands, due to the $B \sim B''$ spin-orbit interaction, can be computed using the CSE model of Ref. 33, and are found to be in good agreement with those estimated using the mixing coefficients of Green and Western (Refs. 22 and 63).