Title
TRIPLET SPLITTING IN THE B3EU--X3Eg-SYSTEM OF S2 DETECTED BY MAGNETIC TUNING OF
A Cr(I) ATOMIC EMISSION LINE

Permalink
https://escholarship.org/uc/item/0mv8h728

Authors
Cuellar, E.
Brown, N.J.

Publication Date
1981-09-01
Submitted to the Journal of Physical Chemistry

Triplet Splitting in the $B^3\Sigma_u^+ - X^3\Sigma_g^-$ System of $S_2$
Detected by Magnetic Tuning of a Cr(I) Atomic Emission Line

E. Cuellar and N.J. Brown

September 1981

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.
For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Triplet Splitting in the $B^3\Sigma_u^- - X^3\Sigma_g^-$ System of $S_2$
Detected by Magnetic Tuning of a Cr(I) Atomic Emission Line

E. Cuellar and N. J. Brown
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

Triplet splitting in the (7,2) band of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ system of $S_2$ has been detected by absorption of a Cr(I) atomic emission line at 3018 Å, using a technique called Tunable Atomic Line Molecular Spectroscopy. The Cr line was split into Zeeman components, and a differential absorption measurement was obtained as a function of magnetic field strength. Five transitions between triplet split levels of $S_2$ were calculated to be nearly resonant with the chromium emission line, and used to interpret the absorption spectrum observed by magnetic scanning. A resolution greater than $6 \times 10^4$ was demonstrated.

This research was supported by the Assistant Secretary for Environment, Office of Environmental Compliance and Overview, Environmental Safety and Engineering Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.
I. INTRODUCTION

The electronic spectrum of $S_2$ has been the subject of numerous investigations\(^1\). Particular attention has been devoted to the extensive $B \ ^3\Sigma^+_u \rightarrow X \ ^3\Sigma^+_g$ system. The coupling of rotation and electronic motions for both $\Sigma$ states, plus the interaction between spins, have the effect that each energy level given by the quantum number $K$ (total angular momentum apart from spin) is split into three levels, $F_1$, $F_2$, and $F_3$, with $J = K + 1$, $K$, and $K - 1$ respectively ($J$ is the total angular momentum quantum number)\(^2\). As a result of this triplet splitting, each band in the $B-X$ system consists of 10 branches: six main branches for which $\Delta K = \Delta J$, and four satellite branches for which $\Delta K \neq \Delta J$\(^3\).

The main branches are denoted by $R_i(K)$ and $P_i(K)$, where $i$ indexes the $F_i$ levels involved. These branches are easily observed in both absorption and in emission using high resolution spectrographs\(^4-7\). The four satellite branches, $T_{R31}$, $N_{P31}$, $R_{P31}$, and $R_{R31}$, are generally weaker\(^8\), and have been observed in emission for some bands of the $B-X$ system by Barrow and co-workers\(^9\). Rotational satellites have also been observed by selectively excited fluorescence, using either an argon ion laser line (5145 Å)\(^10\), or atomic emission lines: Zn (3076 Å) and Cd (3261 Å)\(^11\).

We report here the observation of triplet splitting in the $(7,2)$ band of the $B \ ^3\Sigma^+_u \rightarrow X \ ^3\Sigma^+_g$ system of $S_2$ by absorption of a Cr (I) atomic emission line at 3018 Å. The Cr emission line is split into Zeeman components by placing the light source in a magnetic field. A direct measurement of the $S_2$ absorption in the neighborhood of the Cr atomic emission line is obtained by magnetic tuning of the Zeeman components. In this manner, a high resolution spectrum of $S_2$ can be obtained without the need of a high resolution spectrometer.
Triplet Splitting in the $B^3\Sigma_u^- - X^3\Sigma_g^-$ System of $S_2$

Detected by Magnetic Tuning of a Cr(I) Atomic Emission Line

E. Cuellar and N. J. Brown
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

Triplet splitting in the (7,2) band of the $B^3\Sigma_u^- - X^3\Sigma_g^-$ system of $S_2$ has been detected by absorption of a Cr(I) atomic emission line at 3018 Å, using a technique called Tunable Atomic Line Molecular Spectroscopy. The Cr line was split into Zeeman components, and a differential absorption measurement was obtained as a function of magnetic field strength. Five transitions between triplet split levels of $S_2$ were calculated to be nearly resonant with the chromium emission line, and used to interpret the absorption spectrum observed by magnetic scanning. A resolution greater than $6 \times 10^4$ was demonstrated.

This research was supported by the Assistant Secretary for Environment, Office of Environmental Compliance and Oversight, Environmental Safety and Engineering Division of the U.S. Department of Energy under Contract No. W-7405-ENG-48.
I. INTRODUCTION

The electronic spectrum of $S_2$ has been the subject of numerous investigations. Particular attention has been devoted to the extensive $B \, ^3\Sigma_u^- - X \, ^3\Sigma_g^-$ system. The coupling of rotation and electronic motions for both $\Sigma$ states, plus the interaction between spins, have the effect that each energy level given by the quantum number $K$ (total angular momentum apart from spin) is split into three levels, $F_1$, $F_2$, and $F_3$, with $J = K + 1$, $K$, and $K - 1$ respectively ($J$ is the total angular momentum quantum number). As a result of this triplet splitting, each band in the $B$-$X$ system consists of 10 branches: six main branches for which $\Delta K = \Delta J$, and four satellite branches for which $\Delta K \neq \Delta J$.

The main branches are denoted by $R_i (K)$ and $P_i (K)$, where $i$ indexes the $F_i$ levels involved. These branches are easily observed in both absorption and in emission using high resolution spectrographs. The four satellite branches, $T_{R31}$, $N_{P13}$, $P_{P31}$, and $P_{R13}$, are generally weaker, and have been observed in emission for some bands of the $B$-$X$ system by Barrow and co-workers. Rotational satellites have also been observed by selectively excited fluorescence, using either an argon ion laser line (5145 Å) or atomic emission lines: Zn (3076 Å) and Cd (3261 Å).

We report here the observation of triplet splitting in the (7,2) band of the $B \, ^3\Sigma_u^- - X \, ^3\Sigma_g^-$ system of $S_2$ by absorption of a Cr (I) atomic emission line at 3018 Å. The Cr emission line is split into Zeeman components by placing the light source in a magnetic field. A direct measurement of the $S_2$ absorption in the neighborhood of the Cr atomic emission line is obtained by magnetic tuning of the Zeeman components. In this manner, a high resolution spectrum of $S_2$ can be obtained without the need of a high resolution spectrometer.
The magnetic scanning of a single Zeeman component of an atomic emission line was first used by Bitter and co-workers\textsuperscript{12} for investigating the hyperfine structure and isotope shift of the resonance radiation of mercury. This technique was utilized by Hadeishi and McLaughlin\textsuperscript{13} to develop a new type of atomic absorption spectrometer to detect trace mercury, and utilizing the Zeeman effect for background correction. Zeeman effect based atomic absorption spectrometry (ZAA) has been developed further to include the detection of numerous other atomic species\textsuperscript{14,15}.

Zeeman scanning of molecular line profiles in flames was first demonstrated by Hollander and Broida\textsuperscript{16}. Recently, ZAA spectrometry has been extended to the detection of small molecules which exhibit sharp rotational electronic structure\textsuperscript{17}. This new technique, called Tunable Atomic Line Molecular Spectroscopy (TALMS), has been used to detect NO, NO\textsubscript{2}, SO\textsubscript{2}, and HCHO\textsuperscript{17,18}. We are interested in applying this technique to the detection and measurement of species present in combustion environments such as flames.

II. EXPERIMENTAL

In a magnetic field, an atomic energy level of total angular momentum quantum number \( J \) is split into \( 2J + 1 \) states which are identified by a magnetic quantum number \( M_J \), where \( M_J = J, J-1, \ldots, -J \).\textsuperscript{19} Transitions for which \( \Delta M_J = 0 \) result in the \( \pi \) components of the Zeeman splitting pattern, and are not shifted (or shifted only slightly) from the zero-field value \( \nu_0 \) of the transition. Transitions for which \( \Delta M_J = \pm 1 \) are called the \( \sigma^{\pm} \) components, and are shifted symmetrically to lower and higher energies about \( \nu_0 \). The \( \pi \) and \( \sigma^{\pm} \) components also differ in their polarization. With transverse observation (perpendicular to the direction of the magnetic field), the \( \pi \) components are linearly polarized parallel to the magnetic
field, while the $\sigma^\pi$ components are linearly polarized perpendicular to the field. For longitudinal observation (parallel to the magnetic field), $\pi$ components are not observed, and $\sigma^\pm$ components are circularly polarized: the high frequency $\sigma^+$ component is circularly polarized in a counterclockwise direction, while the low frequency $\sigma^-$ component is circularly polarized in the opposite direction.

The splitting and polarization of spectral lines form the basis for detection of molecules by Tunable Atomic Line Molecular Spectroscopy\textsuperscript{17,18}. By varying the strength of the magnetic field, one of the Zeeman components of the atomic emission line is tuned into coincidence with a sharp transition in the electronic absorption spectrum of the molecule to be detected, in this case $S_2$, while the other component is shifted off resonance. The matching Zeeman component indicates the extent of absorption by $S_2$ plus background absorption due to other species present, while the unmatched component indicates background absorption only. A differential measurement of the absorptions of the matched and unmatched Zeeman components provides a quantitative measurement of the molecule of interest.

A diagram of the experimental apparatus is shown in Figure 1. The light source is a modification of a magnetically confined arc lamp described by Hadeishi and Anderson\textsuperscript{20}. The cathode is made by spot welding several turns of nichrome tape (Tophet C, 16% Cr, 60% Ni, and 24% Fe) to the tip of a stainless steel screw, and the anode is constructed from a modified automobile spark plug. Argon is flowed through the light source at a pressure of less than 2 torr. A d.c. discharge of 50-150 mA to the cathode excites the emission spectrum of Cr, Ni, and Fe simultaneously. The atomic emission passes through a hole drilled in one pole of the electromagnet.
(Varian model V-4004) for longitudinal observation. The light is focused through a 6 cm quartz cell adapted with a finger containing sulfur (sublimed sulfur, Mallincrodt). The finger is heated in an oil bath to \( T_f = 200^\circ C \). At this temperature, the vapor pressure of sulfur is about 2 torr, and is composed principally of the species \( S_8, S_6, S_4, \) and \( S_2^{21,22} \). The cell is heated to \( T_c = 750^\circ C \) to insure that all the sulfur vapor is dissociated into \( S_2^{22} \).

The variable phase retardation plate consists of a block of fused quartz mounted at a 45° angle in a magnetic clamp. The clamp is actuated by a pair of drive coils, and the stress on the quartz block produces a retardation of the phase of the light passing through it. By driving the clamp with an a.c. current, a variable retardation effect is produced, which, in combination with the fixed linear polarizer in front of the monochromator (McPherson model 218, grating blazed at 2000 Å, 1200 grooves/mm), allows for the alternate transmission of the matched and unmatched Zeeman components to the photomultiplier tube (Hamamatsu Type YA7122). The signal is processed electronically and displayed on a strip chart recorder.

III. RESULTS AND DISCUSSION

The emission spectrum obtained by exciting the nichrome tape could be readily assigned to Ni, Cr, and Fe using tables of line spectra of the elements. Several lines in the neighborhood of 3000 Å were found to result in differential absorption signals: Cr at 3000.9, 3005.1, and 3017.6 Å, and Fe at 3008.1 Å. The Cr (I) line at 3017.57 Å was selected because of its higher relative intensity, and was assigned to the transition \( a \, D_3^+ \rightarrow y \, F_4^- \) at 33,129.6 cm\(^{-1}\).
The upper and lower energy levels of this atomic line are split into 9 and 7 new states respectively by the external magnetic field.\textsuperscript{19} The $\Delta M_J = 0, \pm 1$ selection rule results in a total of 21 transitions in three groups of seven closely spaced components, corresponding to $\sigma^-, \pi$, and $\sigma^+$. With the optical axis parallel to the direction of the magnetic field, only the $\sigma^-$ and $\sigma^+$ groups of components appear. The separation between these two groups is $0.088 \text{ cm}^{-1}/\text{kgauss}$, while the separation between the individual components of $\sigma^-$ and $\sigma^+$ is $0.0066 \text{ cm}^{-1}/\text{kgauss}$. Furthermore, at a discharge plasma temperature of 500 K\textsuperscript{18}, the Doppler width (FWHM) of the individual components is $0.074 \text{ cm}^{-1}$. Therefore, the seven closely spaced components that comprise each of $\sigma^-$ and $\sigma^+$ appear as single broad and asymmetric lines, and are not resolved into individual components except at high field strengths.

The dependence of the differential absorption signal due to $S_2$ on the strength of the external magnetic field is shown in Figure 2. As the field is increased the signal decreases and passes through zero at about 8 kgauss. Increasing the field strength further results in differential absorption signals of opposite sign to those obtained at lower fields. This change in polarity implies that at lower field strengths, one of the circularly polarized Zeeman components of the Cr (I) line, $\sigma^+$ or $\sigma^-$, is in resonance with a molecular absorption of $S_2$, while at higher fields, this component falls off resonance while the other $\sigma$ component tunes into a different absorption of $S_2$.

The $\sigma$ components were assigned to the positive and negative differential absorption signals as follows. First, the absorption cell is replaced by a second linear polarizer oriented at 90° to the other polarizer. The variable phase retardation plate is replaced with a block of fused quartz.
mounted in a small vise at 45° relative to the crossed polarizers. Stress is applied until the intensity of the transmitted light is half the intensity transmitted when both polarizers are parallel and no stress is applied to the block. The second linear polarizer is then replaced by the absorption cell, and a 5 kgauss field is applied to the chromium emission line. At this field strength, a positive differential absorption signal is observed, and the transmitted intensities I and I₀ are recorded as the sulfur is heated to constant temperature. The measurement of I/I₀ is repeated with the quartz plate positioned at 90° to the initial orientation, and the entire experiment is repeated at 13 kgauss, where a negative signal is observed. In this manner, it was determined that the positive absorption signals correspond to preferential overlap of the σ-component with an absorption of S₂, while the negative signals result from the overlap of the σ+ component with different absorptions of S₂ at higher frequency.

Interpretation of the magnetic field dependence requires a detailed examination of the electronic spectrum of S₂ in the neighborhood of 3018 Å. The frequency of the Cr (I) atomic line at 33,129.6 cm⁻¹ could overlap with a low K line in the v', v'' = 7,2 band, or with a high K (K'V₆₀) line in the (4,0) band. Rotational analyses of either band have not been published²⁶.

The energy level diagram for K'' = 13 in the (7,2) band of S₂ is shown in Figure 3. The transitions which are allowed between the triplet split levels are also shown. Frequencies for the six main branches and four satellite branches were calculated for K'' = 1 to 60 using the expressions for F₁, F₂, and F₃ given in Reference 2. These expressions are functions of two spin splitting constants, γ and λ, which are functions of the
vibrational quantum number \( v \), and are different for each of the electronic states. Spectroscopic constants for both the \( B^3 \Sigma_u^- \) and \( X^3 \Sigma_g^- \) states were taken from Huber and Hertzberg\(^27\), and \( \gamma \) and \( \lambda \) for the ground state from Barrow and Yee\(^28\). The spin splitting constants for \( v' = 7 \) in the excited \( B \) state, however, are not well known. Meyer and Crosley\(^11\) reported a value of \( \lambda = -4.7 \) for the \( v' = 0, 2, \) and \( 4 \) states, and concluded that \( v' = 7 \) is also inverted (\( \lambda < 0 \)) from published data on bands belonging to \( v' = 7 \). Barrow and du Parcq\(^1\) reported \( \gamma = 0.05 \) for \( v' = 0, 1, \) and \( 4 \). These two values, \( \lambda = -4.7 \) and \( \gamma = 0.05 \), were assumed for \( v' = 7 \) and used to calculate the frequencies of the ten branches in the \((7,2)\) band of \( S_2 \)\(^29\).

Five transitions were calculated to be within 1.5 cm\(^{-1}\) of \( v_o = 33,129.6 \) cm\(^{-1}\), the frequency of the Cr (I) atomic line in the absence of an external magnetic field. These transitions are shown at the top of Figure 4, and are \( R_2 \) (13) at 33,129.4 cm\(^{-1}\), \( P_3 \) (13) at 33,129.7 cm\(^{-1}\), \( R_1 \) (21) at 33,130.0 cm\(^{-1}\), \( R_{31} \) (21) at 33,130.2 cm\(^{-1}\), and \( T_{31} \) (27) at 33,130.6 cm\(^{-1}\). Since the total pressure in the absorption cell is about 2 torr, these absorptions are predominantly Doppler broadened, and have a Doppler breadth (FWHM) of 0.095 cm\(^{-1}\) at 750°C. The relative intensities of these five absorptions were calculated using the results of Tatum and Watson\(^8\).

Figure 4 also shows the Zeeman components of the chromium atomic line at several magnetic field strengths. At 2.5 kgauss, \( \sigma^- \) and \( \sigma^+ \) overlap \( R_2 \) (13) and \( P_3 \) (13) respectively. The differential absorption signal at this field strength is positive (see Figure 2), and is due to the more favorable overlap of \( \sigma^- \). As the field increases, \( \sigma^- \) and \( \sigma^+ \) spread apart, and eventually overlap equally the different absorptions of \( S_2 \); at 8 kgauss, the differential absorption signal is zero. Increasing the field to 12.5
kgauss moves $\sigma^-$ out of resonance with $R_2$ (13), while $\sigma^+$ overlaps first $R_1$ (21) and then $R_{31}$ (21). The absorption signal is negative since the roles of $\sigma^-$ and $\sigma^+$ as monitors of $S_2$ and of background are reversed. The $\sigma^+$ component has a width of about 0.22 cm$^{-1}$ at this field strength, and is too broad to resolve the two $S_2$ absorptions. As the field is increased further to 21 kgauss, the low frequency $\sigma^-$ component remains off resonance with any of the rotational branches of $S_2$ (the next branch is calculated to be $N_{13}$ (9) at 33,127.9 cm$^{-1}$), while $\sigma^+$ begins to overlap $R_{31}$ (27). This overlap results again in a negative differential absorption signal.

IV. CONCLUSIONS

Since a complete experimental rotational analysis of the (7,2) band of $S_2$ is not available, unambiguous assignment of the differential absorption signals shown in Figure 2 to discrete absorptions of $S_2$ is difficult. Nevertheless, the magnetic scanning technique described here is capable of resolving individual branches of the (7,2) band which arise due to triplet splitting in the $B^3E_u - X^3E_g$ system. A resolution better than $6 \times 10^4$ is demonstrated.

Clearly, the Cr emission line at 3018 Å is suitable for the detection of $S_2$ in spite of its complex Zeeman splitting pattern. However, for high resolution spectroscopy and lineshape determination, a better choice would be the Mg (II) line at 2928.63 Å, which was used by Durand to excite the fluorescence spectrum of $S_2$. This line overlaps the $R_1$ (39) transition at 34,135.50 cm$^{-1}$ in the (8,1) band of $S_2$ and can be assigned to the atomic transition $2P_{1/2} - 2S_{1/2}$. In a direction parallel to the magnetic field, the Zeeman splitting pattern for this line consists simply of single $\sigma^-$ and $\sigma^+$ components.
ACKNOWLEDGEMENTS

The authors thank Dr. Tetsuo Hadeishi for many helpful discussions during the course of this work. This research was supported by the Assistant Secretary for Environment, Office of Environmental Compliance and Overview, Environmental Safety and Engineering Division of the U.S. Department of Energy under contract No. W-7405-ENG-48.
REFERENCES

3. In addition to these ten branches, there are also four satellite Q branches: $R_{Q21}$, $R_{Q32}$, $P_{Q12}$, and $P_{Q23}$. These weak satellite branches have not been observed (see ref. 9).


26. The (4,0) and (7,2) bands of the $S_2 B \Sigma_u^+ - X \Sigma_g^-$ system are presently being re-analyzed by R.F. Barrow and co-workers at Oxford (private communication).


29. A similar calculation was performed for the (4,0) band, but the calculated spectrum did not agree with the frequencies determined by magnetic scanning of the Cr line.

30. The $B^3 \Sigma_u^-$ state is strongly perturbed by the $B''^3 \Pi_u$ and $d^1 \Pi_u$ states (J.M. Ricks and R.F. Barrow, Can. J. Phys. 47, 2423 (1969) and ref. 9 and 11), making reliable evaluation of $\lambda'$ and $\gamma'$ very difficult.


32. R.F. Barrow, private communication.

FIGURE CAPTIONS

Figure 1 Schematic diagram of the experimental apparatus: EM electromagnet; S light source; L quartz lens; C absorption cell; VPRP variable phase retardation plate; P polarizer; M monochromator; D detector.

Figure 2 Differential absorption signal due to $S_2$ as a function of the strength of the external magnetic field. The shift of $\sigma\pm$ components is $\Delta V_s = 0.0438$ cm$^{-1}$/k gauss.

Figure 3 Triplet splitting of the rotational levels of $S_2$. The $v'' = 2$ level is normal while the $v' = 7$ level is inverted. The six main branches ($\Delta K = \Delta J$) and four satellite branches ($\Delta K \neq \Delta J$) are shown for $K'' = 13$.

Figure 4 Calculated absorption spectrum of $S_2$ in the neighborhood of 3018 Å. Also shown in the overlap of the $\sigma\pm$ components of the Cr emission line with the $S_2$ absorptions at four magnetic field strengths.
Figure 1
Figure 2
Energy level diagram for $S_2$

\[ B \sum_u \]

\[ X \sum_g \]

$\nu=7$

$\nu''=2$

Figure 3

XBL809-2024
Figure 4
This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.