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A study of the $A^2\Pi$–$X^2\Sigma^+$ and $B^2\Sigma^+$–$X^2\Sigma^+$ band systems of scandium monosulfide, ScS, using Fourier transform emission spectroscopy and laser excitation spectroscopy

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Abstract

Emission spectra of the $A^2\Pi_{3/2}$–$X^2\Sigma^+$ (0, 1), (0, 0), and (1, 0) bands and the $B^2\Sigma^+$–$X^2\Sigma^+$ (0, 1), (0, 0), (1, 0), (2, 0), and (3, 1) bands of ScS have been recorded in the 10 000–13 500 cm^{-1} region at a resolution of 0.05 cm^{-1} using a Fourier transform (FT) spectrometer. The $A^2\Pi_r$–$X^2\Sigma^+$ (1, 0) band as well as the $B^2\Sigma^+$–$X^2\Sigma^+$ (0, 0) and (1, 0) bands have been recorded at high resolution (±0.001 cm^{-1}) by laser excitation spectroscopy using a supersonic molecular beam source. The FT spectral features range up to $N = 148$, while those recorded with the laser cover the "low-N" regions. The lines recorded with the laser exhibit splittings due to the ^{45}Sc ($I = 7/2$) magnetic hyperfine interactions, which are large (~6.65 GHz) in the $X^2\Sigma^+$ state and much smaller in the $B^2\Sigma^+$ and $A^2\Pi$ states. The energy levels were modeled using a traditional 'effective' Hamiltonian approach, and improved spectroscopic constants were extracted and compared with previous determinations and theoretical predictions.

Keywords: Scandium monosulfide; Fourier transform emission; Laser excitation spectroscopy

1. Introduction

Transition metal-containing molecules are species of chemical and astrophysical importance. Diatomic molecules like ScS are simple transition metal-containing systems in which *d*-electrons take part in bonding, and they provide ideal models for the understanding of electronic structure and reactivity. The limited number of valence electrons, small spin–orbit interaction, and single isotope (^{45}Sc with $I = 7/2$), make scandium-containing molecules attractive for theoretical and experimental studies of transition metal chemistry. Bonding and electronic structure information can best be gleaned from comparative studies of isovalent scandium-containing molecules such as scandium monoxide, ScO, and scandium monosulfide, ScS. These two species have intense visible band systems that to a first approximation represent a $4s(\sigma) \rightarrow 3d_{\pm1}/4p_{\pm1}(\pi)$ ($A^2\Pi$-$X^2\Sigma^+$) and $4s(\sigma) \rightarrow 3d_0/4p_0(\sigma)$ ($B^2\Sigma^+$–$X^2\Sigma^+$) promotion [1]. The principal difference between these two molecules lies in the longer and weaker ScS bond [2]. Spectroscopy of transition metal-containing sulfides are also of astrophysical importance, as TiS [3] and ZrS [4] have been tentatively identified in S-type Mira variable stars, and there is strong possibility that other transition metal sulfides such as ScS may also be found. Precise spectroscopic data are necessary for a search for these species in complex stellar spectra.

So far only limited spectroscopic data are available for ScS. Although the $A^2\Pi$–$X^2\Sigma^+$ and $B^2\Sigma^+$–$X^2\Sigma^+$ band systems have been known for several decades [5,6], the spectra of ScS are much less studied than those of ScO. These ScS transitions, which are shifted to the red relative to those of

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ScO, were recorded at near Doppler resolution using conventional emission spectroscopy [5]. The $B^2\Sigma^+$–$X^2\Sigma^+$ (0,0) band was analyzed [6] to produce a set of fine and hyperfine parameters. A liquid nitrogen-cooled hollow cathode discharge source was used, but the low-N lines were not assigned.

Recently the permanent electric dipole moments of the ($v = 1$) $B^2\Sigma^+$ and ($v = 0$) $X^2\Sigma^+$ states were determined from the analysis of the molecular beam optical Stark laser excitation spectra [also called laser induced fluorescence (LIF)] for numerous lines of the $B^2\Sigma^+$–$X^2\Sigma^+$ (1,0) band [7]. The ($v = 1$) $B^2\Sigma^+$ state in [7] was erroneously referred to as the ($v = 0$) $B^2\Sigma^+$ state. A prerequisite for the analysis of the optical Stark spectra was the recording and analysis of the field-free low-N lines of the $B^2\Sigma^+$–$X^2\Sigma^+$ (1,0) band. Only lines having $N'' \leqslant 3$ were included in the analysis. A review of the spectroscopy can be found in [7].

Here, we report on the observation of emission spectra of the $A^2\Pi_{3/2}$–$X^2\Sigma^+$ (0,1), (0,0), and (1,0) bands as well as the $B^2\Sigma^+$–$X^2\Sigma^+$ (0,1), (0,0), (1,0), (2,0), and (3,1) bands using Fourier transform (FT) spectroscopy. We also report on the observation of the $A^2\Pi_r$–$X^2\Sigma^+$ (1,0) band as well as the $B^2\Sigma^+$–$X^2\Sigma^+$ (0,0) and (1,0) bands using molecular beam LIF spectroscopy. A total of 4159 lines were combined in a weighted least squares fit to produce an improved set of spectroscopic parameters for the $B^2\Sigma^+$, $X^2\Sigma^+$, and $A^2\Pi$ states.

2. Experimental

2.1. Fourier transform emission spectroscopy

The FTS emission bands of ScS were observed inadvertently in an experiment intended to search for TiH bands using a commercial high temperature carbon tube furnace. The experiment was intended to produce the TiH bands from the reaction of Ti metal vapor with 160 Torr of H_2 at a temperature of about 2150 °C. In addition to H_2, about 100 Torr of He was also present in the furnace to serve as a buffer gas. The observed spectra were full of bands of the electronic transitions of TiO, TiS, ScF, and ScS. The scandium metal required to produce the Sc-containing molecules was present in the furnace from a previous experiment. The sulfur impurities necessary to make ScS were also present in the furnace from previous metal sulfide experiments.

The spectra in the 8500–16 000 cm^{-1} interval were recorded with the 1-m Fourier transform spectrometer associated with the McMath-Pierce telescope of the National Solar Observatory at Kitt Peak. The spectrometer was equipped with a UV beamsplitter, RG645 red pass filters and midrange silicon diode detectors. The spectra were recorded by co-adding 4 scans in about 45 min of integration at a resolution of 0.05 cm^{-1}. The spectral line positions were determined using a data reduction program called PC-DECOMP developed by Brault. The peak positions were determined by fitting a Voigt lineshape function to each line. The ScS rotational lines were observed with a typical signal-to-noise ratio of 5:1 and have an approximate linewidth of 0.110 cm^{-1}. The rotational lines were calibrated using the measurements of TiO bands [8] also observed in the same spectra, and the measurements are expected to have an accuracy of ±0.007 to ±0.01 cm^{-1} depending upon the signal-to-noise ratio and extent of blending.

2.2. Supersonic molecular beam laser spectroscopy

The LIF measurements of the $A^2\Pi$–$X^2\Sigma^+$ (1,0), $B^2\Sigma^+$–$X^2\Sigma^+$ (0,0), and $B^2\Sigma^+$–$X^2\Sigma^+$ (1,0) bands were performed at Arizona State University. A modified version of the laser ablation/supersonic expansion production scheme used in the previous ScS study [7] was selected for sample preparation. A variable speed rotating Sc metal rod was irradiated by the third harmonic (355 nm) light originating from a Q-switched Nd:YAG laser operating at approximately 1 mJ/pulse and at 20 Hz. Argon gas at a backing pressure of about 2000 kPa flowed over a room temperature sample of carbon disulfide. A commercial solenoid type valve was used to introduce this gas mixture into a nozzle assembly for reaction with the laser-vaporized metal. A 5-mm diameter skimmer, situated approximately 15 cm downstream from the ablation source, separated the two compartments of the differentially pumped chambers of the molecular beam apparatus. Typical operating pressures of approximately 5×10^{-5} and 1×10^{-6} Torr for the source and detection chambers, respectively, were maintained.

The LIF spectra were recorded using a stabilized, single longitudinal mode, continuous wave Ti:sapphire ring laser. Approximately 50 mW of loosely focused laser radiation intersected the molecular beam sample at a 90° angle 10 cm downstream from the skimmer. The resulting LIF was collected and collimated with a lens assembly and directed through a ±10 nm band-pass filter centered at the excitation wavelength. The filtered LIF signal was detected via a cooled photomultiplier tube and processed using gated single-photon counting techniques.

Wavelength calibration of the $B^2\Sigma^+$–$X^2\Sigma^+$ (0,0) ($T_{00} = 12455.7738\ \text{cm}^{-1}$) and $B^2\Sigma^+$–$X^2\Sigma^+$ (1,0)($T_{10} = 12940.3981\ \text{cm}^{-1}$) spectra utilized a heated I_2 cell and the published transition wavenumbers of Gerstenkorn and Luc [9]. The wavelength of the $A^2\Pi$–$X^2\Sigma^+$ (1,0) band system is too red ($T_{10} = 11571.4218\ \text{cm}^{-1}$) for convenient use of the I_2 calibration scheme and a uranium optogalvanic cell was used for calibration. The atomic transition wavenumbers were taken from the Los Alamos atlas [10]. The experimental arrangement described by Sansonetti and Weber [11] was employed. Simultaneous recording of the transmission of two confocal étalons assisted in the required long wavenumber extrapolation from the uranium calibration lines to the ScS LIF features. One étalon, 10 cm in length and thoroughly described in a previous paper [12], was temperature controlled, evacuated, and actively stabilized by monitoring the transmission of a frequency