Transition moments, radiative transition probabilities, and radiative lifetimes for the band systems A $^2\Pi$–X $^2\Sigma^+$, B $^2\Sigma^+$–X $^2\Sigma^+$, and A $^2\Pi$–A´ $^2\Delta$ of scandium monosulfide, ScS

João Gabriel Farias Romeu, Antonio Ricardo Belinassi, Fernando R. Ornellas*

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, São Paulo 05508-000, Brazil

ABSTRACT

A manifold of electronic states of ScS was investigated with special emphasis on the low-lying states X $^2\Sigma^+$, A´$^2\Delta$, A $^2\Pi$, and B $^2\Sigma^+$. For all states, potential energy curves were constructed covering internuclear distances from the equilibrium region through the dissociation limit. For the above states, besides providing the most accurate set of theoretical spectroscopic parameters to date, we have also computed dipole moment functions, transitions dipole moment functions, the associated radiative transition probabilities, and radiative lifetimes. For the states known experimentally, X $^2\Sigma^+$, A $^2\Pi$, and B $^2\Sigma^+$, our results significantly expand our present knowledge of the energetic profile of these states thus providing a new perspective for understanding the limited spectral data for this species known so far. For the new state, A´$^2\Delta$, yet unobserved experimentally, our results are sufficiently reliable and accurate to guide spectroscopists on further studies of this species.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

With a single *d*-electron, diatomic molecules containing scandium are ideal simple systems that can help understand bonding involving transition metals atoms, as in comparative studies of hydrides, oxides, and sulfides. Diatomic systems containing transition metal atoms are expected to have a high density of electronic states with many of them of high spin multiplicity, a fact behind part of the difficulties inherent in the analysis of their spectra. Interest in scandium monosulfide has ranged from high temperature vaporization studies [1] focused on physical properties of the solid-vapor system to spectroscopic-oriented investigations [2–6]. The possibility that ScS also be identified in some variable stars, as was the tentative identification of TiS and ZrS, for example, makes its astrophysical study another challenging problem [7,8].

Experimentally, early in the 1970s, ESR and optical spectra of the ScS and YS molecules were investigated while trapped in solid matrices at 4 K by McIntyre et al. [2]; besides magnetic parameters, this work also yielded an IR band at 554 cm^{-1}. This investigation was followed by the observation and vibrational study of the A $^2\Pi$–X $^2\Sigma^+$ and B $^2\Sigma^+$–X $^2\Sigma^+$ transitions in ScS by Stringat

and Fenot [3]. These authors reported the first set of vibrational constants for the ground state X $^2\Sigma^+$ ($\omega_e = 565.2$ cm^{-1} and $\omega_e x_e \sim 1.8$ cm^{-1}), and the state B $^2\Sigma^+$ ($\omega_e = 488.2$ cm^{-1} and $\omega_e x_e \sim 2.0$ cm^{-1}); a value of 561.5 cm^{-1} for $\Delta G_{1/2}$ was also obtained in that study, reasonably consistent with the above result of McIntyre et al. Spectroscopic parameters for the state A $^2\Pi$ could not be determined due to the lack of sensitivity of the film used in the experiment at the longer wavelengths. A rotational study and hyperfine effects of the (0, 0) band of the B $^2\Sigma^+$–X $^2\Sigma^+$ system of ScS were next reported by Fenot et al. [4]. Hyperfine interactions in ScS were further investigated by Steimle et al. [5] using single mode laser induced fluorescence, as well as the determination of dipole moments by recording transitions in the presence of a variable static electric field. More recently, using a Fourier transform spectrometer and laser excitation spectroscopy, Gengler et al. [6] investigated the 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 in the 10,000–13,500 cm^{-1} region, at a resolution of ±0.05 cm^{-1}. Additionally, by laser excitation spectroscopy using a supersonic molecular beam source, the A $^2\Pi_r$–X $^2\Sigma^+$ (0, 1) band as well as the B $^2\Sigma^+$ – X $^2\Sigma^+$ (0, 0) and (1, 0) bands were also recorded at a high resolution (±0.001 cm^{-1}) by the same authors [6].

Theoretically, the low-lying electronic states X $^2\Sigma^+$, A´ $^2\Delta$, and A $^2\Pi$ of ScS were first investigated by Bauschlicher and Langhoff

* Corresponding author.
E-mail address: frornell@usp.br (F.R. Ornellas).

Table 1
Low-lying $\Lambda + S$ electronic states of the ScS molecule, their dissociation channels, and energy separation at the dissociation limit.

States of separated Atoms	Multiplicity	Molecular states	ΔE (cm^{-1}) Exper.[a]	Theor.
$Sc\ (^2D_g) + S\ (^3P_g)$	2, 4	$\Sigma^+, \Sigma^-(2), \Pi(3), \Delta(2), \Phi$	0	0
$Sc\ (^2D_g) + S\ (^1D_g)$	2	$\Sigma^+(3), \Sigma^-(2), \Pi(4), \Delta(3), \Phi(2), \Gamma$	9 043	10 558
$Sc\ (^4F_g) + S\ (^3P_g)$	2, 4, 6	$\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(3), \Phi(2), \Gamma$	11 509	11 899

[a] Weighted averaged over the multiplets. Ref. [12].

[9] at the single and double excitation configuration interaction (SDCI) level of theory using as reference the HF-SCF wavefunction. Additionally, more extensive correlation effects were included using the coupled-pair functional (CPF) approach. Spectroscopic parameters (R_e, T_e, ω_e), and the dipole moment (μ) and the dipole moment derivative ($d\mu/dR$) at the equilibrium distances were reported for the states known experimentally at the time and the new state, A′ $^2\Delta$ yet to be observed; no potential energy curves were reported in this study. In another investigation focusing only on the ground states of transition metal oxides and sulfides, new values of R_e, ω_e, and D_0 calculated at several different levels of theory were reported by Bauschlicher and Maitre [10]. More recently, Halabi and Korek [11] also reported *ab initio* calculations for the electronic states of ScS but some of their results differ considerably from what is known experimentally. For instance, in the Franck-Condon region they locate the state A $^2\Pi$ higher than the B $^2\Sigma^+$ state; also their predicted value for the equilibrium distance of the state A $^2\Pi$ overestimates the experimental one by 0.546 a$_0$, what is not acceptable.

In this work, for the first time, we present an overall picture of a manifold of doublet electronic states of the ScS molecule by reporting potential energy curves covering the equilibrium region through the dissociation limit. For the lowest-lying states known experimentally, and the new A′ $^2\Delta$ state, yet to be investigated, sets of associated spectroscopic parameters, and dipole moment functions were determined. For the transitions A $^2\Pi$–X $^2\Sigma^+$, B $^2\Sigma^+$–X $^2\Sigma^+$, A $^2\Pi$–A′ $^2\Delta$ transition moment functions and transition probabilities and radiative lifetimes were computed. By presenting reliable results for the electronic structure and spectroscopic parameters of the states known experimentally, and expanding our present spectroscopic knowledge about this system, we hope this study can motivate and guide future experimental investigations on this and related molecules.

2. Methods

The closeness of the energy levels of transition metal atoms makes the characterization of diatomic systems containing these elements a much more challenging problem than with main group elements. In the case of ScS, considering only the three lowest dissociation channels, Table 1 lists 69 allowed molecular states that correlate with the states of the atomic species as predicted by the Wigner-Witmer rules [13]. Although we are mainly interested in transitions involving the four lowest molecular states of doublet multiplicity, to construct properly the potential energy curves (PEC) for these states, thus avoiding discontinuities especially as the internuclear distance increases, one necessarily needs to include all doublet states correlating with the channels shown in Table 1, as it will become apparent shortly.

To describe all these states, a first step accounting for static correlation effects was to carry out state averaged complete active space self-consistent field (SA-CASSCF) [14,15] calculations by distributing nine electrons into a ten orbitals active space (5, 2, 2, 1). This active space includes the (3d, 4s) orbitals of scandium and the (3s, 3p) of sulfur. The active space notation implies that we

are working in the C_{2v} point group, a subgroup of the $C_{\infty v}$ point group, due to computer code design restrictions that allow only Abelian groups. The correspondence between the representations in the $C_{\infty v}$ and C_{2v} point groups is: $A_1(\Sigma^+, \Delta_{x^2-y^2})$, $B_1(\Pi_x)$, $B_2(\Pi_y)$, $A_2(\Sigma^-, \Delta_{xy})$. There are at all 36 unique doublet states to describe in the state averaged CASSCF calculation. However, to guarantee the symmetry equivalence of both π_x and π_y orbitals, and that additionally Δ states appear in both A_1 and A_2 symmetries, the Φ states in both B_1 and B_2 symmetries, and the Γ states appear in the A_1 and A_2 symmetries, the total number of states in fact mixed was 61 (16A$_1$, 15B$_1$, 15B$_2$, 15A$_2$). The number of configuration state functions (CSF) generated in this step was: 6996 for A_1 symmetry, 6920 for B_1/B_2, and 6884 for A_2. The incorporation of dynamic correlation into the final wavefunctions was done by allowing all single and double electron excitations on top of the reference spaces generated in the previous step. For such, we used the internally contracted version of the multireference configuration interaction (MRCI) method [16,17] implemented in the Molpro suite of programs [18]. The dimensions of the MRCI wavefunction reached about 8.3 million CSFs for all symmetries. Due to this computationally demanding step, we restricted the extraction of eigenvalues of the Hamiltonian matrix to the 10 lowest roots of each symmetry. The basis functions employed in the expansion of the molecular orbitals were the all-electron correlation consistent sets (cc-pV5Z) for scandium [19] and sulfur [20].

The energies obtained for each symmetry include the Davidson correction (+Q), which estimates the contribution of the missing higher excitations needed to reach the full configuration interaction limit [21,22]. Calculations were carried at 43 internuclear distances covering the interval from the equilibrium region to the dissociation limit. Then they were interpolated and used as numerical potentials in the solution of Schrödinger radial equation for the nuclear motion using the Intensity program [23]. Using standard fitting procedures described elsewhere [13,24–27], sets of spectroscopic parameters were determined for the four lowest states. Radiative transition probabilities as expressed by the Einstein spontaneous emission coefficients, $A_{v',v''}$ (in s^{-1}), and given below for the case of rotationless potentials,

$$A_{v',v''} = 7.2356 \times 10^{-6} |D_{v',v''}|^2 \nu_{v',v''}^3 \frac{(2 - \delta_{0,\Lambda'+\Lambda''})}{(2 - \delta_{0,\Lambda'})}.$$

were also evaluated with the Intensity program. We note that in this expression, $\nu_{v',v''}$ is the transition energy, and $(2 - \delta_{0,\Lambda'+\Lambda''})/(2 - \delta_{0,\Lambda'})$ is the degeneracy factor [28,29]. As implemented in the Intensity program, the multiplication constant is the appropriate factor to express the probabilities in s^{-1}, when the transition moment is given in units of eÅ, and the energy in cm^{-1}. In this expression, $D_{v',v''}$ stands for the transition dipole moment operator matrix element evaluated as

$$D_{v',v''} = <v'|D(R)|v''>$$

where $|v'>$ and $|v''>$ represent the upper and lower state vibrational wavefunctions, and $D(R)$ is the transition dipole moment function evaluated over the whole range of internuclear distances at the MRCI level of theory. Radiative lifetimes were eval-