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Electronic structure and spectroscopic properties of the scandium monosulfide, ScS

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Abstract: Scandium, with a single d-electron, has a referential role in understanding and studying the electronic structure and reactivity of systems involving transition metals atoms. Diatomic systems containing transition metals atoms, such as monoxides and monosulfides, besides their intrinsic chemical relevance, are also important in astrophysical studies, since there are detections of some oxides and sulfides in variable stars [1,2]. Nevertheless, in the case of scandium monosulfide, ScS, there are very few spectroscopic data available in the literature, including those determined through experimental and theoretical studies. Moreover, the high density of electronic states relatively close to the lowest-lying states hinders its analysis and characterization, making the investigation of diatomic systems containing transition metals elements much more challenging comparatively to other diatomic molecules.

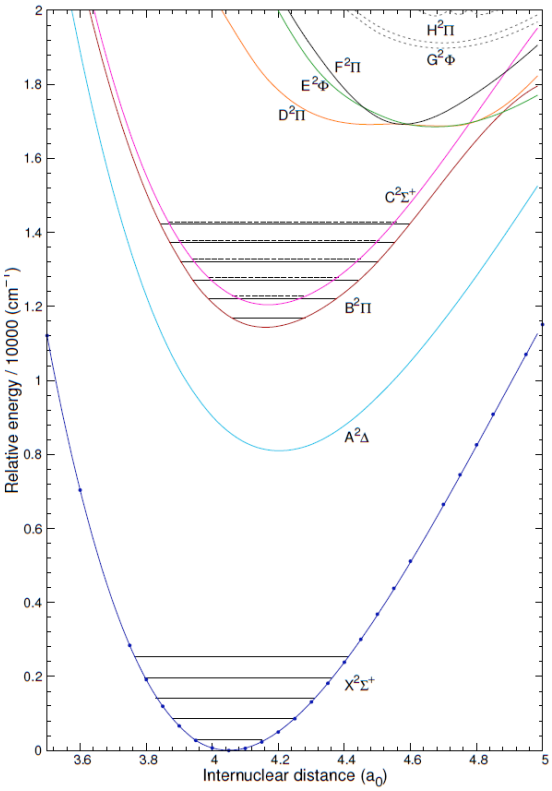

Fig. 1. PEC associated to the lowest-lying states near equilibrium region.

Our theoretical approach to describe the electronic states makes use of the state-averaged complete active space self-consistent field (SA-CASSCF) [3, 4] and the multireference configuration interaction (MRCI) [5, 6] methods, both implemented in the Molpro suite of programs [7], and a cc-pV5Z basis set [8, 9]; all doublet states associated to the two lowest-lying dissociation channels were calculated.

In the present work, a characterization of the doublet electronic states of the ScS molecule associated with the lowest-lying dissociation channels is presented via potential energy curves (PEC) from the equilibrium region to the dissociation limit and the associated set of spectroscopic parameters. The closeness of the second and the third dissociation channels gives rise to difficulties in describing the electronic states at higher energies, but does not influence the description of the major states investigated in this study,

which are shown in Fig. 1, including their associated vibrational levels. For the ground state, X $^2\Sigma^+$, the prediction of ω_e equal to 569.8 cm^{-1} shows a very good agreement with the experimental one, 565.2 cm^{-1} [10], a significant improvement relative to the theoretical ones of 608 cm^{-1} and 503 cm^{-1}, using single and double excitation configuration interaction (SDCI), and coupled-pair functional (CPF) approaches, respectively. For the C $^2\Sigma^+$ state, the set of constants (R_e, ω_e, T_e) of (4.169 a_0, 503 cm^{-1}, 12 040 cm^{-1}) is also quite concordant with those obtained experimentally (4.1596 a_0, 488.74 cm^{-1}, 12 455.77 cm^{-1}) [11]. For the new $^2\Delta$ state, predicted theoretically [12], with values of T_e and ω_e varying from 6803 to 8996 cm^{-1} and from 488 to 513 cm^{-1}, respectively, according to the methodology employed, are also well described; for the T_e and ω_e parameters, are values of 8086 cm^{-1} and 504 cm^{-1}, respectively, are expected to be much more reliable than existing ones. All the four states studied are very polar, showing an increasing polarity in the order X $^2\Sigma^+$ < C $^2\Sigma^+$ < B $^2\Pi$ < A $^2\Delta$. Besides the electronic transitions for the systems, B $^2\Pi$ – X $^2\Sigma^+$, C $^2\Sigma^+$ – X $^2\Sigma^+$, we also report the one for the B $^2\Pi$ – A $^2\Delta$ transition. With the transition moment functions, we also evaluated transition probabilities and radiative lifetimes, thus improving significantly the characterization of this system.

Considering the reliability of the results obtained in this study in describing experimentally known states and the new ones, it is expected that this investigation can guide and motivate additional experimental and theoretical investigations involving this molecule and related systems in the future, by providing new data and new tools to approach similar diatomic molecules calculations.

Key-words: Spectroscopy, ab initio methods, electronic states, scandium monosulfide, CASSCF/MRCI.

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