Theoretical electronic structure of the molecule SrCl for the feasibility of laser cooling

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Abstract. Electronic structure of the molecule SrCl has been investigated by employing the ab initio methods CASSCF/MRCI+Q with Davidson correction in the representation \(2\Sigma^{\pm}\), neglecting spin-orbit effects, and using the computational program Molpro. The potential energy curves of the low-lying doublet and quartet electronic states have been investigated. The harmonic vibrational wave number \(\omega_e\), the relative electronic energy \(T_e\), referred to the ground state, the rotational constant \(B_e\) and the equilibrium internuclear distance \(R_e\), have been calculated for the investigated electronic states. Moreover, the static dipolar moments have been determined in term of the internuclear distance \(R_e\).

1. Introduction
Because of their wide-ranging applications in many areas, the strontium monohalides SrX have received considerable attention from both experimentalists and theoreticians. The Strontium monohalide molecules are present in sunspots, SC-stars, cool M-giant stars, stellar red-giant stars, and in S-type stars [1]. The abundances of these species are important for understanding the evolutionary phases, activities and interactions of the stars with cometary material [2]. Since the SrX molecules are produced in the gaseous phase at high temperature, it is very difficult to realize such experimental measurement at high temperature to produce these molecules and observe their spectra [3, 4]. Therefore, theoretical studies are quite useful for the experimentalists to identify the electronic structures and their corresponding spectroscopic constants.

The alkaline earth mono-halides all have diagonal Franck–Condon Factors (FCFs) and are, in principle, amenable to laser cooling. While many of these molecules are studied experimentally [5-7], there is absence of the study of the electronic structure of the molecules SrX, particularly for the higher excited electronic states. Shuman et al. [8] introduced the first direct cooling of a polar molecule (SrF) by using an optical cycling scheme with Doppler and Sisyphus cooling forces. This significant innovation needs deep knowledge of the electronic structure and its ro-vibrational energy levels of the ultracold candidate molecules. Moreover, highly diagonally distributed FCFs and the short radiative lifetimes (between \(10^{-6}\) and \(10^{-9}\) s) are needed for these ultracold molecules. While the FCF calculation is based on the accurate potential energy curve of two electronic states, the radiative lifetimes need the calculation of the dipole moment.

DeMill [9] has detailed a prototype design for quantum computation using ultracold polar molecules, trapped in a one-dimensional optical lattice, partially oriented in an external electric field, and coupled by the dipole-dipole interaction. This offers a promising platform for quantum computing because scale-up appears feasible to obtain large networks of coupled qubits.
The spectra of alkaline earth monohalides have been frequently investigated in the literature [10-16] by using various theoretical and experimental spectroscopic techniques. For the molecule SrCl, the $A^2\Sigma^+ - X^2\Sigma^+$ transition has been observed and analysed by Brinkmann et al. [17], Singh et al. [18], and Schröder et al. [19], while the transition $B^2\Sigma^+ - X^2\Sigma^+$ has been reported by Ernest and Schröder [20].

In the present work, the theoretical electronic structure of SrCl molecule is investigated, using $ab$-initio methods. The potential energy curves (PECs) are plotted, the electronic energy with respect to the ground state $T_e$, the harmonic frequency $\omega_e$, the rotational constant $B_e$, the internuclear distances at equilibrium $R_e$ and the static dipole moments, have all been calculated.

2. Computational methods

Electronic structure of the molecule SrCl has studied by using Multi-Configuration Self-Consistent Field (MCSCF) methods [21]. This generation is followed by the Multi Reference Configuration Interaction (MRCI+Q) technique, with Davidson correction $+Q$ [22]. These calculations have been performed employing the computational chemistry program MOLPRO [23], using the graphical user interface GABEDIT [24]. For the strontium atom, Sr, the basis set is an Effective Core Potential; ECP28MWB [25], choosing 28 inner electrons in the core. The chlorine atom is taken as an all electrons scheme with the basis aug-cc-pVQZ;c (augmented correlation consistent polarized valence quintet zeta). Therefore, 27 electrons will remain in the valence shells for an SrCl molecule. The active space contains 18 active orbitals corresponding to 6σ[Sr: 5s, 4d0, 5p0, 6s; Cl: 3p0, 4s0], 3π[Sr: 4d±1, 5p±1;Cl: 3p±1] and 1δ[Sr: 4d±2] distributed as 6a1, 3b1, 3b2, and 1a2 noted [6,3,31] in the irreducible representation of the C2v point group. We choose to freeze 20 electrons among the 27 free electrons for this molecule. This implies that 7 valence electrons are considered in the MRCI calculation and used for the excitation to the different active orbitals.

3. Results and discussion

The SrCl molecule is assumed to be ionic Sr$^+$Cl$^-$. Our computational calculations have been done for the first lowest 5 electronic states of the SrCl molecule. The theoretical energies as functions of the internuclear distance $R_e$, varying from 1.88 Å to 3.08 Å, have been calculated. The ground state is $X^2\Sigma^+$, and the lowest excited electronic states are all found located below 35100 cm$^{-1}$. The potential energy curves of these electronic states are given in Figure 1.

![Figure 1. Potential energy curves of the molecule SrCl.](image-url)

Theoretical energy values, $T_e$, the spectroscopic constants $\omega_e$ and $B_e$, as well as the internuclear distance at equilibrium, $R_e$, are represented in the Table 1, along with different experimental and theoretical results given in the literature.
Comparison of our calculated values of $T_e$ with those obtained experimentally in the literature [9, 13, 19], shows very good agreement with the relative difference $0.54\% \leq \Delta T_e/T_e \leq 5.6\%$. For the internuclear distance, $R_e$, our theoretical values are very significant, since the relative difference from those obtained experimentally in the literature [9, 13, 19] shows excellent agreement with the value $1.2\% \leq \Delta R_e/R_e \leq 2.3\%$. While for the $\omega_e$ and $B_e$ constants, the relative differences show very good agreement with the experimental data [9, 13, 19] with relative differences $1.2\% \leq \Delta \omega_e/\omega_e \leq 2.3\%$ and $1.2\% \leq \Delta B_e/B_e \leq 2.3\%$, respectively. One can notice that for the majority of the investigated electronic states, good agreement with the published data in the literature. This confirms accuracy of the new data given in Table 1.

![Figure 2](image_url)

**Figure 2.** Dipole moment curves of the molecule SrCl.

For the study of the bond nature and the polarity of the molecule SrCl, we show in Figure 2, the variation of the static dipole moment of this molecule in terms of the internuclear distance $R$ by taking the Sr atom at the origin. Note that the dipole moment curves are in the negative region and that the sign convention corresponds to the polarity of Sr$^+$Li$^-$. Moreover, these dipole moment curves
increase in the negative region, which points out polarized states that dissociate into ionic fragments. Note also the linear trend of the static dipole moment curves in the negative region. This behaviour of a bond from such curve can be understood by using the Pacchioni et al. method [26]. For two electric charges +q and −q separated by the internuclear distance Re, the dipole moment curve is a straight line if the compound formed by the two charges is ionic, and curved if the compound has a dominating covalent character.

4. Conclusion
As implemented in the use of ab-initio/MRCI+Q calculations, the adiabatic potential energy and the dipole moment curves for the low-lying electronic states of SrCl molecule have been calculated. From the plots of these curves the spectroscopic constants Re, ωe, Te, and Be, are determined for the bound electronic states. Comparing the obtained values with the available data, both theoretical and experimental, shows very good agreement, which confirms the validity and the accuracy of the newly investigated constants in the present work. These data can lead to the calculation of the Franck-Condon factor, which demonstrate feasibility of laser cooling of the molecule SrCl.

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