Chemical Physics 485–486 (2017) 29–34

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

# A theoretical study on laser cooling of silicon monofluoride

Wensha Xia [a,b], Mingkai Fu [a,b], Haitao Ma [a,*], Wensheng Bian [a,b,*]

[a] Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

*Article history:*
Received 13 August 2016
In final form 16 January 2017
Available online 19 January 2017

*Keywords:*
SiF
Laser cooling
*Ab initio*

ABSTRACT

The feasibility of direct laser cooling of silicon monofluoride (SiF) is investigated and assessed using the internally contracted multireference configuration interaction method with the Davidson correction and entirely uncontracted aug-cc-pwCV5Z basis sets. As for the $A^2\Sigma^+(v'=0) \rightarrow X^2\Pi$ transition, the computed radiative lifetime is 0.69 μs and the vibrational branching ratio $R_{v'v}$ is highly diagonally distributed with the $R_{00}$ being 0.994, which are desirable for rapid and efficient laser cooling. In addition, good agreement is achieved between our computed spectroscopic properties and the available experimental data for the $X^2\Pi$ and $A^2\Sigma^+$ states of SiF. We propose a kind of laser cooling scheme, in which the wavelengths are located in the visible region. Both our calculated Doppler and recoil temperatures are of the order of μK, and the calculated minimum distance necessary to bring the velocity of a SiF beam to that suitable for trapping is 13 cm, indicating that the SiF molecule can be cooled to the ultracold regime through the proposed scheme.

## 1. Introduction

Nowadays Laser cooling of atomic systems is a rather well-established experimental technique. However, molecular laser cooling constitutes a relatively new field, which had been considered practically impossible for many years and so far much less experience is available [1–7]. In particular, the ultracold fluorine-containing molecules promise exciting applications in quantum computation, electron electric dipole moment and controlled molecular dynamics [7–10]. Since the first successful direct laser cooling was achieved in the SrF molecule by Shuman et al. [11] using just three laser beams, there have been a lot of efforts made to develop new cooling schemes [12–17]. More recently, Hummon et al. and Zhelyazkova et al. succeeded in achieving the translational laser cooling for YO [15] and CaF [16] by laboratory experiments. According to previous investigations [17–19], a suitable laser-cooling candidate must meet three criteria: highly diagonal vibrational branching ratio, a short lifetime and no interference from intermediate electronic states.

Recently, with the development of theoretical chemistry, quantum chemical calculations have been successfully used in addressing optical issues [19,20]. In particular, several diatomics such as hydrides and halides were identified as the possible laser-cooling candidates theoretically [13,14,17,19,21–23]. Here, by means of highly accurate *ab initio*and dynamical calculations, we explore a feasible cooling cycle from the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition of the silicon monofluoride (SiF) system, and find that SiF is a promising candidate for laser cooling. Although the direct laser cooling for the SiF molecule has not been reported, the spectroscopic properties on SiF have attracted a great deal of research interests [24–36]. Experimentally, in 1976 the radiative lifetime of the $A^2\Sigma^+$ state for SiF was measured for the first time[24]. Later, Saito et al. observed the microwave spectrum of SiF and reported the molecular constants of the $X^2\Pi$ state [25]. Tanaka et al. measured the vibrational spectrum of SiF by an infrared diode laser spectrometer [32]. On the theoretical side, some theoretical studies on SiF have been reported [33–36]. In 1971, Hare et al. [33] performed CF calculations on the ground state at the equilibrium internuclear separation. Later, the analysis about the first eight lowest states of SiF was carried out using the configuration interaction methods [34]. Rydberg-type orbitals were included (4s for the $A^2\Sigma^+$, 3d for the $C^2\Delta$ state) to account for the energy of these states and the Rydberg character of the $A^2\Sigma^+$ state was discussed. The ground state of SiF was also investigated by Garrison et al., who determined the bond energies using the generalized valence bond and dissociation-consistent configuration interaction methods [35]. Recently, the spectroscopic properties for the $X^2\Pi$ and $a^4\Sigma^-$ states of SiF were studied by Shi et al. [36] with an accurate treatment for the core-

---

* Corresponding authors at: Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China (H. Ma and W. Bian).

*E-mail addresses:* mht@iccas.ac.cn (H. Ma), bian@iccas.ac.cn (W. Bian).

http://dx.doi.org/10.1016/j.chemphys.2017.01.007
0301-0104/

valence and relativistic corrections. However, in the previous theoretical studies, some calculated spectroscopic constants evidently deviate from experiment, and several detailed properties such as the vibrational branching ratio of lowest doublet–doublet transition have not been determined. Here, we propose the schemes for the viable laser cooling cycle, which is a theoretical exploration for the direct laser cooling of the nonmetallic compound. Our work also elucidates the detailed electronic structures and the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition of SiF.

This article is organized as follows. The theoretical methods and computational details are described in Section 2. In Section 3, we present the results and discussion, and propose the schemes for the laser cooling of SiF. The conclusions are given in Section 4.

## 2. Methods and computational details

In this work, we present an extensive theoretical study on SiF molecule based upon the highly accurate *ab initio* calculations, which are performed using the MOLPRO 2008.1 program package [37]. It is important to generate balanced orbitals for use in subsequent correlation calculations, so state-averaged complete active space self-consistent field (CASSCF) [38] calculations are carried out for the orbital optimization using the orbitals obtained with the Hartree–Fock method as the starting guess. Then, utilizing the CASSCF energies as reference values, the energies of each electronic state are computed by the internally contracted multireference configuration interaction method (icMRCI), which can describe a large amount of correlation energy via single and double electron excitations [39], and further correlation energy due to higher excitations is approximated by the Davidson correction (+Q) [40]. Two reference states are used for generating the internally contracted pairs in the icMRCI procedure. Scalar relativistic effects are included using the second-order Douglas-Kroll scalar relativistic correction. The spin–orbit coupling (SOC) effects are introduced by the state interaction approach with the full Breit-Pauli Hamiltonian [41]. As for the basis sets, the rather large entirely uncontracted augmented correlation consistent weighted core-valence basis sets (aug-cc-pwCV5Z) [42,43], which adequately describe both core-core and core-valence correlations, are chosen for both Si and F atoms. The selection of active space is crucial in the CASSCF and icMRCI + Q calculations [44,45]. Here various active spaces in CASSCF calculations have been tested then the active space, which consists of eight orbitals: three *2p* on F and one *3s*, three *3p* with one additional *4s* orbital of Si, is referred to as (9e, 8o) and chosen for the further calculations. The active space (9e, 8o) is also used for the subsequent icMRCI calculations, and this choice is sufficient to describe the $X^2\Pi$ and $A^2\Sigma^+$ states of the SiF accurately. Notice that the *2s* electrons of F are put into the closed shell, which means that the F *2s* orbital is doubly occupied in all reference configuration state functions, but are still correlated in the icMRCI calculations to account for the core-valence correlations. The rest of the inner electrons are kept frozen and not correlated.

To obtain accurate potential energy curves (PECs), all *ab initio* calculations are performed with the resolution of 0.025 Å for bond lengths in important regions, while in other regions coarser grids of 0.05–0.1 Å are used. The small step is adopted around the equilibrium region so that the properties of the PECs could be displayed more clearly.

The Einstein spontaneous emission coefficient $A_{v'v}$ is evaluated by the following expression [46,47]

$$A_{v'v} = \frac{16\pi^3}{3\varepsilon_0\hbar}\frac{S(J',J)}{2J'+1}v^3|\Psi_{v'J'}|M(r)|\Psi_{vJ}|^2$$

where $A_{v'v}$ is in units of $s^{-1}$, $M(r)$ is the transition dipole function in units of Debye (denoted as D for short), $\varepsilon_0$ is the vacuum permittivity in units of $F \cdot cm^{-1}$, $\hbar$ is the reduced Planck constant, $v$ is emission frequency in units of $cm^{-1}$, $S(J',J)$ is the Hönl-London rotational intensity factor, $\Psi_{v'J'}$ and $\Psi_{vJ}$ are normalized radial wave functions, respectively. The radiative lifetime $\tau$ of the transition can be calculated using the following formula,

$$\tau = 1/\sum_{v} A_{v'v}$$

The nuclear Schrödinger equation is solved using Le Roy's LEVEL program [48] to obtain the spectroscopic parameters for the $X^2\Pi$ and $A^2\Sigma^+$ states, including the equilibrium bond length ($R_e$), the harmonic vibrational constant ($\omega_e$) and the rotational constant ($B_e$).

## 3. Results and discussion

### 3.1. PECs and spectroscopic constants

The main configurations of $X^2\Pi$ and $A^2\Sigma^+$ states at $R_e$ are listed in Table 1. The ground state for SiF is the $X^2\Pi$ state, the main configuration of which is Si $3s^2(3p_x$ or $3p_y)^1$ + F $2p_x^2 2p_y^2 2p_z^2$. The second lowest state here is the $A^2\Sigma^+$ state, whose main configuration is Si $3s^2 3p_z^1$ + F $2p_x^2 2p_y^2 2p_z^2$. Indeed, the $X^2\Pi$ and $A^2\Sigma^+$ states are not dominated by the single ionic configuration or covalent configuration. The PECs of the two states computed using the icMRCI + Q method are shown in Fig. 1. The weights of ionic configuration in the $A^2\Sigma^+$ and $X^2\Pi$ states decrease gradually with the increase of the internuclear distances, as a result of which both states correlate to the neutral atomic Si($^3$P)+F($^2$P) limit. The energy of $A^2\Sigma^+$ state is more than 20,000 $cm^{-1}$ higher than that of the $X^2\Pi$ state at $R_e = 1.6000$ Å from our calculation.

Since the spectroscopic properties of the $X^2\Pi$ and $A^2\Sigma^+$ states have been investigated in experiment, a comparison of our results with experimental values could provide an indicator of the reliability and accuracy of our calculations. As seen in Table 2, we present our calculated spectroscopic constants, together with previous theoretical and experimental values for comparison. Some improvements are found in the icMRCI + Q results compared to the icMRCI ones, although the calculated spectroscopic constants by the icMRCI method have been in good agreement with the experimental values.

As for the $X^2\Pi$ state, our calculated $R_e$ and $\omega_e$ are 1.6000 Å and 856.0 $cm^{-1}$ respectively, better agreement with experiment data (1.6011 Å and 857.19 $cm^{-1}$) [31] compared to that reported from the previous calculations (1.658 Å and 858.83 $cm^{-1}$) [36]. We consider that the deviation by Shi et al. [36] arises from the neglect of 4s electron effect in the Si atom. Concerning the $A^2\Sigma^+$ state, the experimental $T_e$ is 22858.3 $cm^{-1}$ [31], whereas our calculated $T_e$ is 22909.8 $cm^{-1}$, indicating that the deviation between our results and experiment is only 52 $cm^{-1}$, which is a dramatic improvement compared to the previous result (31,073 $cm^{-1}$) [34]. Our calculational results also provide much improved $R_e$ and $\omega_e$ values

**Table 1**
The main configuration of the lowest two Λ–S states at individual $R_e$.

| State | Main configuration[a] |
|---|---|
| $X^2\Pi$ | Si $3s^2(3p_x$ or $3p_y)^1$ + F $2p_x^2 2p_y^2 2p_z^2$ |
| $A^2\Sigma^+$ | Si $3s^2 3p_z^1$ + F $2p_x^2 2p_y^2 2p_z^2$ |

[a] The main configuration of bound states are obtained from the analysis of the icMRCI wavefunctions and illustrated by the occupation of active electrons.