A Theoretical Study on Laser Cooling Feasibility of Group IVA Hydrides XH (X = Si, Ge, Sn, and Pb): The Role of Electronic State Crossing

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The feasibility of direct laser cooling of SiH, GeH, SnH, and PbH is investigated and assessed based upon first principles. The internally contracted multi-reference configuration interaction method with the Davidson correction is applied. Very good agreement is obtained between our computed spectroscopic constants and the available experimental data. We find that the locations of crossing point between the $B^2 \Sigma^-$ and $A^2 \Delta$ states have the tendency of moving downwards from CH to SnH relative to the bottom of the corresponding $A^2 \Delta$ potential, which precludes the laser cooling of GeH, SnH, and PbH. By including the spin-orbit coupling effects and on the basis of the $A^2 \Delta$ $\rightarrow$ $X^2 \Pi^3/2$ transition, we propose a feasible laser cooling scheme for SiH using three lasers with wavelengths varying from 400 to 500 nm, which features a very large vibrational branching ratio (0.9954) and a very short radiative lifetime (575 ns). Moreover, similar studies are extended to carbon monosulfide (CS) with a feasible laser cooling scheme proposed. The importance of electronic state crossing in molecular laser cooling is underscored, and our work suggests useful caveats to the choice of promising candidates for producing ultracold molecules.

Keywords: laser cooling, ab initio, spin-orbit coupling, electronic state crossing, group IVA hydrides

1. INTRODUCTION

Laser cooling of diatomic molecule is an issue of great interest owing to their promising applications in many fields such as quantum computing and precision measurement (Carr et al., 2009; Hudson et al., 2011; Yan et al., 2013; Baron et al., 2014). Direct laser cooling of SrF molecules to $\mu$K level was firstly achieved with only three laser beams (Shuman et al., 2010). In addition, transverse and longitudinal laser cooling experiment was applied to YO (Hummon et al., 2013) and CaF (Zhelyazkova et al., 2014), respectively. So far only a few molecules including SrF, CaF, and YO have been cooled to the ultracold temperature experimentally, and there is an urgent need to search for more suitable molecular candidates for laser cooling. Recently, a number of theoretical efforts have been made in searching for promising molecular laser cooling candidates (Wells and Lane, 2011a; Fu et al., 2016a; Cao et al., 2019; González-Sánchez et al., 2019; Xu et al., 2019). It is generally accepted (Di Rosa, 2004; Fu et al., 2016b) that, a suitable laser-cooling candidate must meet the
The paper is organized as follows. The theoretical methods and computational details are briefly described in section 2. The results and discussion are shown in section 3. The conclusions are given in section 4.

2. METHODS AND COMPUTATIONAL DETAILS

In this paper, all the \textit{ab initio} calculations of SiH, GeH, SnH, and PbH are performed using the MOLPRO 2012.1 program package (Werner et al., 2012). For each \Lambda-S state, the energies are computed using the complete active space self-consistent field (CASSCF) (Werner and Knowles, 1985) approach followed by the icMRCI+Q (Langhoff and Davidson, 1974). The lowest electronic configuration of Si is (core)3s23p6 corresponding to the atomic states 3P and 1D. In combination with the 1s function of a H atom, the lowest electronic configuration of SiH in X1Σg+ is invariably (core)4σ25σ26σ02π1 and the next is (core)4σ25σα6σ092π2 leading to the multiplets 4Σ−, 2Σ+, and 2Σ−, which could be considered as involving a πσ → ππ transition within the Si atom. In asymptote region, the 5σ molecular orbital origins from the 1s on hydrogen, while the 6σ and 2π correspond to the 3p on silicon.

The choice of active space is very important in the CASSCF and MRCl+Q calculations (Liu et al., 2009; Yu and Bian, 2011, 2012). The active space of SiH used here consists of ten orbitals corresponding to Si 2p3s3p4p and H 1s, and is referred to as (1s1e, 10o), which is carefully chosen to include proper orbitals, and large enough for the present calculations. Our test calculations indicate that the full valence space is inadequate, and thus additional five orbitals are added into the active space. The inner shell orbitals are included to account for the core-valence correlation effects and the outer virtual orbitals are added to give a better description on the dissociation behavior and Rydberg character, especially for excited electronic states (Shen et al., 2017).
et al., 2017). In fact, a completely satisfactory set could neither be found by increasing the active orbital space nor by including more states (Simah et al., 1999). The best compromise we could achieve is to distribute the eleven electrons in 10 active orbitals. As for the basis set, we use the aug-cc-pV5Z basis sets for Si and H atom. In the SOC calculations, the SO eigenstates are obtained by diagonalizing $\hat{H}^el + \hat{H}^SO$ in the basis of eigenfunctions of $\hat{H}^el$. In addition, the $\hat{H}^el$ and $\hat{H}^SO$ are obtained from the icMRCI+Q calculations and icMRCI+Q waves functions, respectively. The active space for GeH in the present work is (9e, 9o), which consists of the Ge 3d $\pi$ 4s $\pi$ 5p $\sigma$ and H 1s orbitals. The accuracy and computational performance are compromised, thus the active space of GeH includes the 3d $\pi$ orbitals, valence orbitals and 5p $\sigma$ orbitals. The aug-cc-pV5Z-DK basis sets are used for GeH. Here, the active space for SnH consists of the Sn 4d5s5p and H 1s orbitals. We use the aug-cc-pVQZ basis sets for H and aug-cc-pwCVQZ-PP with ECP60MDF effective core potentials for Sn. Similarly, the active space for PbH is (15e, 10o), which consists of the Pb 5d6s6p and H 1s orbitals. We use the aug-cc-pVQZ basis sets for H and aug-cc-pwCVQZ-PP with ECP60MDF for Pb. In addition, the active space used for the study of CS is (10e, 8o) corresponding to the C 2s2p and S 3s3p, and we use the aug-cc-pV5Z basis sets for both C and S atoms.

The Einstein spontaneous emission coefficient $A_{\nu'\nu}$ is calculated by the following expression (Herzberg, 1950),

$$A_{\nu'\nu} = \frac{16\pi^2 S(J', J)}{3\epsilon_0 \hbar} \nu^3 |\Psi_{\nu',J}|^2 |M(r)| |\Psi_{\nu,J}|^2$$

(1)

where $A_{\nu'\nu}$ is in units of s$^{-1}$, $\epsilon_0$ is the vacuum permittivity in units of F cm$^{-1}$, $M(r)$ is the transition dipole function in Debye unit, $\nu$ is emission frequency in units of cm$^{-1}$, $\Psi_{\nu',J}$ and $\Psi_{\nu,J}$ are normalized radial wave functions, $\hbar$ is the Planck constant and $S(J', J)$ is the Hönl-London rotational intensity factor. The radiative lifetime for a given vibrational level $\nu'$ can be obtained by the following equation,

$$\tau_{\nu'} = \frac{1}{\sum_{\nu} A_{\nu'\nu}}$$

(2)

The spectroscopic parameters of group IVA hydrides, including the equilibrium bond length ($R_e$), the harmonic vibrational constant ($\omega_0$), the rotational constant ($B_r$), and adiabatic relative electronic energy referred to the ground state ($T_e$) are obtained using the Le Royv’s LEVEL program (Le Roy, 2007).

3. RESULTS AND DISCUSSION

3.1. PECs of the $\Lambda$-S States and Spectroscopic Constants

For the group IVA hydrides, the main configuration of the ground state ($X^2\Pi$) is (core)$4\sigma^25\sigma^26\sigma^02\pi^1$. The second lowest state here is the $A^2\Delta$, whose main configuration is (core)$4\sigma^25\sigma^16\sigma^02\pi^2$. The PECs of SiH, GeH, SnH, and PbH computed using the icMRCI+Q method are shown in Figures 1–4, respectively. The weights of ionic configuration in the $X^2\Pi$ and $A^2\Delta$ states decrease gradually with increasing internuclear distances. As seen in Figure 1, the five states of SiH correlate to the three dissociation limits. The $X^2\Pi$ and $A^2\Delta$ states are the two energetically lowest lying electronic state and correlate to the neutral atomic Si($^3\Pi$)+H($^3S$) limit and Si(1D)+H($^3S$) limit, respectively. From Figures 2–4, we can see that the $X^2\Pi$ and $A^2\Delta$ states of GeH, SnH, and PbH correlate to the neutral atomic Ge/Sn/Pb($^3\Pi$)+H($^3S$) limit and Ge/Sn/Pb($^1D$)+H($^3S$) limit, respectively. The PEC of the $B^2\Sigma^-$ crosses with that of $A^2\Delta$ will be discussed in details in section 3.2. The PECs of the $B^2\Sigma^-$ and $X^2\Pi$ correlate to the same neutral atomic Si($^3\Pi$)+H($^3S$) limit.

Since the spectroscopic constants of the $X^2\Pi$ and $A^2\Delta$ states have been measured in experiment for SiH, GeH, SnH, and PbH, comparing with experimental data could provide an indicator of the reliability of our calculations. We present our calculated
spectroscopic constants of SiH, GeH, and SnH in Tables 1, 2 and Table S1, together with previous theoretical and experimental values for comparison. The calculated \( R_e \) and \( \omega_e \) of the \( \chi^2 \Pi \) of SiH are 1.5200 Å and 2047.71 cm\(^{-1} \), respectively, which are in good agreement with the corresponding experiment data (1.5201 Å and 2041.80 cm\(^{-1} \)) (Huber and Herzberg, 1979). The contributions from non-valence orbitals to correlation energy are relatively small for the ground state, however, they become very important for the excited states and lead to noticeable differences. In particular, the experimental \( T_e \) is 24300.4 cm\(^{-1} \) (Huber and Herzberg, 1979) and our calculated one with a better active space is 24299.20 cm\(^{-1} \), whereas that obtained by Zhang et al. (2018) is 25080.92 cm\(^{-1} \), which deviates from experimental value by about 780 cm\(^{-1} \). When additional virtual orbitals are taken into account by Kalemos et al. (2002), the deviation is reduced to around 200 cm\(^{-1} \). The spectroscopic constants of GeH obtained from the active space (9e, 9o) are shown in Table 2. The calculated \( R_e \) and \( \omega_e \) of the \( \chi^2 \Pi \) of GeH are 1.5885 Å and 1902.32 cm\(^{-1} \), respectively, which are in very good agreement with the corresponding experiment data (1.5872 Å and 1900.38 cm\(^{-1} \)) (Towle and Brown, 1993). The \( \chi^2 \Delta \) state of GeH is in very good agreement with the experimental value (534 ± 23 ns) (Bauer et al., 1984). The \( \chi^2 \Delta \rightarrow \chi^2 \Pi \) transition of GeH is listed in Table S2. The calculated radiative lifetime for the \( \chi^2 \Delta(\nu' = 0) \) state of SiH is 613 ns, which is in very good agreement with the experimental value (534 ± 23 ns) (Bauer et al., 1984). The FCIs \( f_{\nu'\nu} \) of the \( \chi^2 \Delta \rightarrow \chi^2 \Pi \) transition for GeH are calculated and plotted in Figure S2. In this work, the \( f_{00} \) (0.995) of SiH is in excellent agreement with the value (0.994) derived from experiment (Smith and Liszt, 1971). The computational value of \( f_{00} \) for GeH (0.940) is in very good agreement with the experimental value 0.928 (Erman et al., 1983).

| State         | Method | \( T_e \) (cm\(^{-1} \)) | \( R_e \) (Å) | \( \omega_e \) (cm\(^{-1} \)) | \( \nu^a \) | \( T_r \) (cm\(^{-1} \)) | \( B_e \) (cm\(^{-1} \)) | \( \mu_e \) (Debye) |
|---------------|--------|--------------------------|-------------|----------------------------|--------|--------------------------|---------------------|------------------|
| \( \chi^2 \Pi \) | This work | 1.5200 | 2047.71 | 0 | 1018.07 | 7.5083 | 0.1451 |
|               |        | 1 | 2996.15 | 2 | 4904.97 |
| Expt.         |        | 1.5201 | 2041.80 | 7.4996 |
| Expt.         |        | 1.5197 | 2042.52 | 7.5039 |
| Calc.         |        | 1.5223 | 2043.15 | 7.4779 |
| Calc.         |        | 1.5223 | 2046.91 | 7.4779 |
| Calc.         |        | 1.5154 | 2043.47 | 7.7258 |
| A\( ^2 \Delta \) | This work | 24299.20 | 1859.72 | 0 | 25277.40 | 7.5164 | 0.134 |
|               |        | 1 | 26968.69 | 2 | 28486.89 |
| Expt.         |        | 24300.4 | 1.5234 | 1858.90 | 7.4664 |
| Expt.         |        | 24255.51 | 1.5198 | 7.5027 |
| Calc.         |        | 24923.56 | 1.546 | 1797 | 7.253 | 0.118 |
| Calc.         |        | 24129.60 | 1.5240 | 1853.15 |
| Calc.         |        | 24323.28 | 1.5148 | 1857.63 | 7.5021 |

\( a \) The vibrational levels are represented by \( \nu \).

\( b \) Huber and Herzberg (1979).

\( c \) Betencourt et al. (1968).

\( d \) Kalemos et al. (2002).

\( e \) Shi et al. (2008).

\( f \) Shi et al. (2013).

\( g \) Ram et al. (1998).

\( h \) Lewerenz et al. (1983).
### 3.2. The Comparison of the Feasibility of Laser Cooling for Group IVA Hydrides

There are some similar properties of group IVA hydrides. The inner closed-shell orbitals are occupied with 2, 10, 28, 46, and 78 electrons for CH, SiH, GeH, SnH, and PbH, respectively. The equilibrium bond length $R_e$ increases regularly from CH to PbH, while the harmonic constant $\omega_0$ decreases in the order of CH $>$ SiH $>$ GeH $>$ SnH $>$ PbH (Huber and Herzberg, 1979; Alekseyev et al., 1996; Zhao et al., 2017). The comparison of the feasibility of laser cooling for group IVA hydrides is summarized in Table 2. An amplified view of crossing regions of PECs for SiH, GeH, SnH, and PbH is shown in Figure 6, we see that the dissociation energies of the $A^2\Delta$ states of SiH, GeH, SnH, and PbH are 7735.89, 4465.21, 2849.26, and 798.36 cm$^{-1}$, respectively. This trend is consistent when the second-row CH is included and the corresponding dissociation energy is 16641.68 cm$^{-1}$ (Wells and Lane, 2011b). The depths of the $A^2\Delta$ state decrease from CH to PbH, and it supports only one vibrational level for PbH. In equilibrium region, two electrons anti-parallelly are distributed on one $(n_p\uparrow n_p\downarrow)$ and two $(n_p\uparrow n_s\downarrow)$ sp$^3$ hybridized orbitals for the $B^2\Sigma^-$ and $A^2\Delta$ states, respectively. The hybridized orbital effect vanishes as the internuclear distance increases to the asymptotic region. Where, $n_p\uparrow n_s\downarrow$ goes to $X(\Pi)$ and $n_p\downarrow n_p\downarrow$ goes to $X(\Delta)$. Therefore, there is a crossing point between the $B^2\Sigma^-$ and $A^2\Delta$ states of group IVA hydrides. The electronic state crossing between the $B^2\Sigma^-$ and $A^2\Delta$ states can lead to nonradiative transition (Wu et al., 2019), and may cause predissociation. This kind of electronic state crossing in a diatomic molecule will become potential energy surface intersections in the polyatomic cases involving multiple electronic states (Liu et al., 2003; Zhao et al., 2006). We find that the locations of crossing point between the $B^2\Sigma^-$ and $A^2\Delta$ states have the tendency of moving downwards from CH to SnH relative to the bottom of the corresponding $A^2\Delta$ state potential. The locations of crossing point between the $B^2\Sigma^-$ and $A^2\Delta$ states of GeH and SnH are 591 and 255 cm$^{-1}$ lower than the corresponding vibrational level $\nu = 0$ in the $A^2\Delta$, while that of third-row SiH is 670 cm$^{-1}$ higher than the vibrational level $\nu = 0$ in the $A^2\Delta$. This trend is consistent when the second-row CH is included since the corresponding crossing point is 3000 cm$^{-1}$ higher (Wells and Lane, 2011b).

The location of crossing point between the $B^2\Sigma^-$ and $A^2\Delta$ states of SiH is higher than the vibrational level $\nu = 0$ in the $A^2\Delta$, indicating that laser cooling of SiH in the $A^2\Delta \rightarrow X^2\Pi$ transition may not be affected by electronic state crossing. However, our results imply that the crossing between the $B^2\Sigma^-$ and $A^2\Delta$ states of GeH will lead to predissociation of all vibrational levels of the $A^2\Delta$ state, which is backed up by experiments of Erman et al. (1983) using high frequency deflection technique. They reported that, 80–90% of the GeH molecules excited to the $A^2\Delta$ state decay via predissociation to their ground state atomic constituents, and fewer than 20% of the molecules follow the regular decay route to the ground state. Furthermore, the $A^2\Delta$ states of SnH and PbH have a similar problem to that of GeH, although there has been no relevant experimental measurements reported. It is clear that GeH and SnH can not be used for laser cooling due to the electronic state crossing. In addition, the small Franck-Condon factor $f_{00}$ (0.08) of PbH also suggests that it is not suitable for laser cooling.

It seems that both CH and SiH are very good laser cooling candidates, and we make a comparison in the following. The $f_{00}$ of SiH (0.995) is close to that of CH (0.9957) (Wells and Lane, 2011b). The radiative lifetimes of the $A^2\Delta$ state of SiH and CH are 575 and 536 ns (Wells and Lane, 2011b), respectively. The $T_{\text{Doppler}}$ and $T_{\text{ recoil}}$ of SiH ($6.65$ and $3.89 \mu$K) are also similar to that of CH ($7.13$ and $7.91 \mu$K) (Wells and Lane, 2011b).

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### Table 2: Spectroscopic constants of the $A^2\Delta$ and $X^2\Pi$ states for GeH.

| State Method | $T_e$ (cm$^{-1}$) | $R_e$ (Å) | $\omega_0$ (cm$^{-1}$) | $v_a$ (cm$^{-1}$) | $T_r$ (cm$^{-1}$) | $B_r$ (cm$^{-1}$) | $\mu_o$ (Debye) |
|--------------|-----------------|----------|------------------------|-----------------|-----------------|-----------------|-----------------|
| $X^2\Pi$     | This work       | 1.5885   | 1902.32                | 0               | 943.46          | 6.7107          | 0.1076          |
|              | Expt.$^b$       | 1.5872   | 1900.38                | 1               | 2777.80         | 4546.19         |
|              | Expt.$^c$       | 1.5880   | 1833.77                | 2               | 6.7269          |                 |
|              | Calc.$^d$       | 1.5823   | 1914.93                |                | 0.097           |                 |
| $A^2\Delta$  | This work       | 1.6100   | 1308.62                | 0               | 26159.92        | 6.5408          | 0.257           |
|              | Expt.$^e$       | 25454    | 1185.15                | 1               | 23780.21        | 28307.39        |
|              | Calc.$^f$       | 26663    | 1.66                   | 2               | 6.535           |                 |
|              | Calc.$^g$       | 25774    | 1.617                  | 3               | 6.5343          | 0.356           |

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$^a$The vibrational levels are represented by $v$.

$^b$Erwin and Brown (1993).

$^c$Huber and Herzberg (1979).

$^d$Chapman et al. (1988).

$^e$Li et al. (2015).
calculated pump and repump wavelengths for SiH and CH are all in the visible region. The electronic state crossing between the $B^2\Sigma^+$ and $A^2\Delta$ states of CH is higher than that of SiH, with both crossing points located above the corresponding vibrational $v' = 0$ levels in the $A^2\Delta$ state. Generally speaking, a larger atomic mass difference for the diatomic candidate is desirable by experimentalists, and in this respect, SiH is better than CH. Furthermore, we will propose a scheme using two spin-orbit states for SiH in the next section, which is more feasible than the one using two $\Lambda-S$ states for CH. The $A^2\Delta \rightarrow X^2\Pi$ transition of CH was used to establish a laser cooling scheme, and the SOC effects were not included (Wells and Lane, 2011a). With the inclusion of the SOC effects into the icMRCI wave functions in our calculations, accurate $\Omega$ states are determined. The calculated spectroscopic constants of SiH are in very good accordance with experimental measurements. The prospect for the production of ultracold SiH molecules by means of direct laser cooling method is discussed below.

### 3.3. Laser Cooling Scheme for SiH

When the SOC effects are taken into account, seven $\Omega$ states, involving four states with $\Omega = 1/2$, two states with $\Omega = 3/2$ and one state with $\Omega = 5/2$, are generated from the five $\Lambda-S$ states of SiH. The PECs of the $\Omega$ states are depicted in Figure 7. The SOC splitting of the $X^2\Pi$ and $A^2\Delta$ states of SiH is shown in Table 3. As seen, the energy separation of the $X^2\Pi_{3/2}$ and $X^2\Pi_{1/2}$ is 140.18 cm$^{-1}$ in this work, which is in excellent agreement with the experimental value (142.83 cm$^{-1}$) (Huber and Herzberg, 1979). For the $A^2\Delta_{3/2}$ and $A^2\Delta_{5/2}$ states, the energy separation is 3.01 cm$^{-1}$.

We find that, the $A^2\Delta_{5/2} \rightarrow X^2\Pi_{3/2}$ transition is suitable for laser cooling in three possible transitions, $A^2\Delta_{3/2} \rightarrow X^2\Pi_{1/2}$, $A^2\Delta_{3/2} \rightarrow X^2\Pi_{3/2}$, and $A^2\Delta_{5/2} \rightarrow X^2\Pi_{3/2}$. In the $A^2\Delta_{5/2} \rightarrow X^2\Pi_{3/2}$ transition, SiH molecules will jump from the $X^2\Pi_{3/2}(v = 0)$ to the $A^2\Delta_{5/2}(v' = 0)$, then the $A^2\Delta_{5/2}(v' = 0)$ state will decay to the $X^2\Pi_{3/2}$ rather than $X^2\Pi_{1/2}$ according to the selection rules. The $A^2\Delta_{5/2} \rightarrow X^2\Pi_{3/2}$ transition can ensure a closed-loop cooling cycle, while the other two transitions can not. The three-laser cooling scheme proposed in the following using the $A^2\Delta_{5/2} \rightarrow X^2\Pi_{3/2}$ transition is more feasible than the one proposed by Zhang et al. (2018) without including the SOC effects. More importantly, they did not consider the effect of electronic state crossing, and proposed a laser cooling cycle for SiH involving the $v' = 1$ vibrational level of the $A^2\Delta$ state, which would predissociation before the radiative transition and can not be used to establish laser cooling cycles.

**Figure 6** | An amplified view of crossing regions of potential energy curves for SiH (A), GeH (B), SnH (C), and PbH (D).
The TDMs of SiH for the $A^2 \Delta_{5/2} \rightarrow X^2 \Pi_{3/2}$ transition at the icMRCI+Q level are represented in Figure 8. The TDMs of SiH is 0.6157 D at $R_e$. The FCFs values of the $A^2 \Delta_{5/2} \rightarrow X^2 \Pi_{3/2}$ transition for SiH are computed and shown in Figure 9. As seen, the $\Delta \nu = 0$ transitions are significantly larger than those for the off-diagonal terms. The present value of $f_{00}$ (0.9949) is so large that the spontaneous decays to $\nu = 1,2$ vibrational levels in the $X^2 \Pi_{3/2}$ are significantly restrained. Additionally, the relative strengths of the photon loss pathways are more directly related to the vibrational branching ratios than the FCFs in the laser cooling cycle (Lane, 2015). Furthermore, we calculate the Einstein A coefficients $A_{\nu'\nu}$ and vibrational branching ratios $R_{\nu'\nu}$ of the $A^2 \Delta_{5/2} \rightarrow X^2 \Pi_{3/2}$ transition for SiH. The $A_{\nu'\nu}$ and $R_{\nu'\nu}$ of the $A^2 \Delta_{5/2} \rightarrow X^2 \Pi_{3/2}$ transition are listed in Table 4. As seen in Table 4, a very large $A_{00}$ ($1.73 \times 10^6$ s$^{-1}$) and very low scattering probabilities into off-diagonal bands ($R_{01} = 3.61 \times 10^{-3}$, $R_{02} = 9.83 \times 10^{-4}$, $R_{03} = 9.20 \times 10^{-8}$) of SiH contribute to a desirable condition for rapid and efficient laser cooling. It should be noted that $R_{00}$ (0.9954) is slightly larger than $f_{00}$ (0.9949), indicating that the probability of spontaneous decay to the $X^2 \Pi_{3/2}(\nu = 0)$ increases when the variations in transition wavelength are taken into account.

The vibrational branching ratios $R_{\nu'\nu}$ is determined by the following expression:

$$ R_{\nu'\nu} = \frac{A_{\nu'\nu}}{\sum_{\nu} A_{\nu'\nu}} $$

TABLE 3 | The spin-orbit coupling (SOC) splitting for SiH.

| State          | Method | SOC splitting(cm$^{-1}$) |
|----------------|--------|-------------------------|
| X1/2, (1)3/2   | This work | 140.18                  |
|                | Expt.$^a$ | 142.83                  |
|                | Calc.$^b$ | 141.12                  |
|                | Calc.$^c$ | 118.5                   |
|                | Calc.$^d$ | 141.0343                |
| (2)3/2, (1)5/2 | This work | 3.01                    |
|                | Expt.$^a$ | 3.85                    |
|                | Calc.$^b$ | 5.19                    |
|                | Calc.$^c$ | 0.1                     |
|                | Calc.$^d$ | 2.7136                  |

$^a$Huber and Herzberg (1979).
$^b$Shi et al. (2013).
$^c$Li et al. (2008).
$^d$Zhang et al. (2018).
Moreover, the Doppler temperature \( T_{\text{Doppler}} \) is the achievable minimum temperature of translational cooling with the Doppler method, it is obtained by the following expression:

\[
T_{\text{Doppler}} = \frac{h}{(4k_B \pi \tau)},
\]

where \( k_B \) and \( h \) are Boltzmann’s constant and Planck’s constant, respectively (You et al., 2016). The radiative lifetime \( \tau \) for the \( A^2 \Delta_{5/2}(v' = 0) \rightarrow X^2 \Pi_{3/2}(v = 0) \) transition of SiH is 3.89 \( \mu \)K.

The proposed scheme to facilitate the laser cooling of SiH is shown in Figure 10. The large \( R_\nu \) (0.9954) of SiH indicates that the \( A^2 \Delta_{5/2}(v' = 0) \rightarrow X^2 \Pi_{3/2}(v = 0) \) transition has the largest probabilities. A desirable laser cooling cycle needs to solve the vibrational branching loss. Therefore, the off-diagonal vibrational branching ratios \( R_\nu \) of SiH are calculated, and the probabilities of decay from the \( A^2 \Delta_{5/2}(v' = 0) \) to the \( X^2 \Pi_{3/2}(v = 1, 2) \) are firstly obtained \( (R_{01} = 3.61 \times 10^{-3} \) and \( R_{02} = 9.83 \times 10^{-4} \)). Besides, the probabilities of the unwanted decay channels are also computed by using \( R_{03} + R_{02} \times R_{13} + \). The negligible value of \( 1.0 \times 10^{-5} \) means that the present scheme will allow for at least \( 1.0 \times 10^5 \) photons absorption/emission cycles, which are sufficient enough to decelerate SiH in a cryogenic beam, in principle (Shuman et al., 2010). The laser cooling scheme takes the transition \( A^2 \Delta_{5/2}(v' = 0) \leftrightarrow X^2 \Pi_{3/2}(v = 0) \) as the main pump, \( A^2 \Delta_{5/2}(v' = 0) \rightarrow X^2 \Pi_{3/2}(v = 1) \) and \( A^2 \Delta_{5/2}(v' = 0) \rightarrow X^2 \Pi_{3/2}(v = 2) \) as the first and second vibrational repump, respectively. Accurate \( T_c \) is crucial for estimating the pump and repump wavelengths in laser cooling cycles, and our calculated \( T_c \) values, which are very close to experimental ones, give confidence in the subsequent study on laser cooling, especially, for SiH. The calculated value of wavelength \( \lambda_{01} \) should be larger than \( \lambda_{00} \), however, the wavelengths \( \lambda_{01} \) obtained by Zhang et al. (2018), is 376.88 nm, which is smaller than that of their main pump.

In our laser-driven cycling, the calculated pump and repump wavelengths of \( \lambda_{00}, \lambda_{01}, \) and \( \lambda_{02} \) are 412.6, 449.7, and 491.8 nm, respectively. The required wavelengths are all in the range of 400–500 nm and can be produced with the frequency doubled semiconductor laser, which has been used for the laser cooling experiment of the strontium atom (Wang et al., 2009). The SiH molecules will stay in the laser cooling cycle until the decay to \( v' \geq 3 \) \( (X^2 \Pi_{3/2}) \).

### 3.4. Laser Cooling Scheme for CS

We further find that CS is a promising candidate based on the criteria mentioned above. The PEGs of CS, obtained at the icMRCI+Q level, is shown in Figure 11. Our calculated \( R_c \) and \( \omega_c \) of the \( \chi^1 \Sigma^+ \) of CS are 1.5380 Å and 1288.63 cm\(^{-1} \), respectively, which are in very good accordance with the corresponding experimental values (1.5349 Å and 1285.1 cm\(^{-1} \)) (Huber and Herzberg, 1979). As for the \( A^2 \Delta \) state of CS, our calculated \( T_c \) 39175.96 cm\(^{-1} \) is in agreement with the experimental value 38,904 cm\(^{-1} \) (Huber and Herzberg, 1979). The calculated vibrational branching ratio \( R_{00} \) is 0.885, which is highly diagonal.

As shown in Figure 11, the PEC of \( A^1 \Pi \) crosses with those of two other electronic states, however, from an amplified view of the crossing regions we see that, the two crossing points are higher than the \( v' = 0 \) vibrational level of the \( A^1 \Pi \) state. So this kind of crossing would not affect laser cooling cycles using the \( A^1 \Pi(v' = 0) \rightarrow \chi^1 \Sigma^+(v' < 3) \) transition. A suitable laser cooling scheme using the \( A^1 \Pi \rightarrow \chi^1 \Sigma^+ \) transition of CS is proposed and
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Ab initio and dynamical calculations are performed, and the calculated spectroscopic constants are in very good agreement with the available experimental data. We find that the locations of crossing point between the $B^2\Sigma^-$ and $A^1\Delta$ states have the tendency of moving downwards from CH to SnH relative to the bottom of the corresponding $A^1\Delta$ potential, and this would lead to failure of cooling GeH and SnH. The potential wells of the $A^1\Delta$ state of group IVA hydrides become shallower and shallower from CH to PbH, with the Franck-Condon factor decreasing, which results in a very small Franck-Condon factor for PbH. It is clear that PbH is not a suitable candidate for laser cooling either. We further propose a practical and efficient laser-cooling scheme for SiH using the $A^1\Delta \rightarrow X^2\Pi_3/2$ transition. The calculated excitation energy is 24299.20 cm$^{-1}$, which is in perfect agreement with the experimental data (24300.4 cm$^{-1}$). This allows us to accurately estimate the pump and repump wavelengths in laser cooling cycles, which is shown to vary from 400 to 500 nm and are easily accessible in experiment. The Doppler temperature and recoil temperature of SiH for the $A^1\Delta \rightarrow X^2\Pi_3/2$ transition are 6.65 and 3.89 $\mu$K, respectively. The computed radiative lifetime is 575 ns, and the vibrational branching ratio is highly diagonally distributed with the $R_{00}$ being 0.9954. Furthermore, we performed additional calculations, and find that, the carbon monosulfide (CS) is a promising candidate which meets the four criteria, and we further propose a suitable laser cooling scheme. We hope that this work will be helpful in searching for promising candidates for producing ultracold molecules.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are available within the article and from the corresponding author on request.

AUTHOR CONTRIBUTIONS

DL carried out the MRCI calculations. DL, MF, HM, and WB analyzed the data and interpreted the results. ZD and CC provided computing assistance. DL, HM, and WB developed

4. CONCLUSIONS

The fourth criterion for molecular laser cooling is proposed in this work, that is, there is no electronic-state crossing, or the crossing point is high enough in energy. Its importance is demonstrated by investigating the laser cooling feasibility of group IVA hydrides and carbon monosulfide.
the theoretical scheme and wrote the paper. WB supervised the research and proposed the fourth criterion for molecular laser cooling.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2020.00020/full#supplementary-material

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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