be expected to be much longer and $\Phi_{\text{isc}}$ smaller than for the other diazanaphthalenes. This is clearly not observed experimentally. However, even small out-of-plane distortions of this molecule which destroy the inversion center can give rise to significant contributions to the $1\pi^* \rightarrow 3\pi^*$ spin-orbit coupling.

An alternative explanation of the short $\tau_{\text{isc}}$ and nonnegligible $\Phi_{\text{isc}}$ concerns the identity of the $S_1$ state in 1,5-naphthyridine. Recent reports provide strong evidence that the lowest excited singlet has $1B_g$ symmetry, a conclusion also reached earlier by Perrins. Alternatively, this state has been assigned as $1A_u$. Spin–orbit–matrix elements calculated from Hückel wavefunctions using the method of ref 6 indicated that coupling between this $1A_u(1n\pi^*)$ state and $3B_{1g}(3\pi^*)$ state would be even stronger than that observed in quinoxaline. Therefore, if $1A_u(1n\pi^*)$ were the lowest singlet state of 1,5-naphthyridine, the molecule would be expected to undergo intersystem crossing with approximately unit efficiency. Since this is not observed, and based on the thoroughness of the spectroscopic treatments, we confirm that the lowest singlet state is $1B_g$ and that out-of-plane vibrations are responsible for the observed nonzero triplet formation in 1,5-naphthyridine.

In 1,8-naphthyridine, calculations based on INDO wave functions indicate that the spin–orbit coupling matrix elements are small, but finite, in this molecule. This would lead one to predict that intersystem crossing will be observed, but that it will not be highly efficient. This result is indeed observed, although singlet photochemistry may be a complicating factor in this case.

It is interesting to note that while the values of the $k_{\text{isc}}$ rate constants for the diazanaphthalenes studied show significant variation from molecule to molecule, as well as in the case of phthalazine in different solvents, the values of the $k_{\text{isc}}$ rate constants are, within experimental error, the same. Although admittedly based on a limited data set, this observation is not unreasonable since all of these molecules have similar $S_1$ states ($1n\pi^*$) at approximately the same energy above the ground state.

**Acknowledgment.** We wish to thank Dr. A. Gupta of the Jet Propulsion Lab for loaning us the gas chromatography column. We thank Professors W. Okamura and R. C. Neuman of this department for the use of their gas chromatographs. We appreciate several helpful discussions with Dr. R. Anderson of Xerox Corp. We wish to thank Ms. L. DeLucci for typing the manuscript. One of us (T.A.S.) was supported during Summer 1979 by the National Science Foundation's Undergraduate Research Participation Program.

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**Electronic Structure of C–Li, Si–H, and Si–Li in the Lowest $4\Sigma^-$ and $2\Pi$ States**

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We have studied the electronic structure of C–Li, Si–Li, and Si–H in the $4\Sigma^-$ and $2\Pi$ states using ab initio SCF, MCSCF, and CI techniques. We find that, while Si–H is similar to C–H, having a $2\Pi$ ground state with the $4\Sigma^-$ approximately 36 kcal mol$^{-1}$ higher, both C–Li and Si–Li have $4\Sigma^-$ ground states with the $2\Pi$ being 33 and 14 kcal mol$^{-1}$ higher, respectively. Potential energy curves and spectroscopic constants are presented for the three title molecules, and some speculation as to the possible consequences of the $4\Sigma^-$ ground state of Si–Li and C–Li is indulged in.

**Introduction**

Recent work in this laboratory resulted in the prediction that the ground state of C–Li is of $4\Sigma^-$ symmetry with the companion $2\Pi$ state 33 kcal $\text{mol}^{-1}$ higher. This is to be contrasted with the C–H situation in which the $2\Pi$ is the ground state, some 17 kcal $\text{mol}^{-1}$ below the $4\Sigma^-$.

In addition, contour maps of the GVB orbitals of C–Li, in both the $4\Sigma^-$ and $2\Pi$ are characteristic of a highly polar molecule with the $4\Sigma^-$ being more polar. A physical picture consistent with the above is that the $4\Sigma^-$ state results from the transfer of an electron from Li to the empty p orbital of carbon, forming C$^-$ which is then stabilized in the field of Li$^+$. In the $2\Pi$ state the transfer is not as favorable, being to a carbon p orbital which already hosts one electron.

The purpose of this report is to explore this idea by determining the $4\Sigma^-$, $2\Pi$ separation in Si–Li and Si–H. Since Si is less electronegative than C, we expect the charge transfer to be less in Si–Li than in C–Li but in the proper direction to differentially favor the $4\Sigma^-$ state. The results

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of our detailed calculations are in accord with this expectation and suggest that, while the $^\text{II}$ is the ground state of Si–H with the $^\Sigma^-$ 36 kcal mol$^{-1}$ higher, the $^\Sigma^+$ is the ground state of Si–Li, being 14 kcal mol$^{-1}$ below the $^\text{II}$.

**Background**

It is surprising that, in spite of the formal similarity of Si–H to C–H and the astrophysical importance of both, relatively few theoretical investigations of its electronic structure have been published. Jordan$^8$ used a semi-empirical approach to calculate the low-lying excited states of Si–H at the ground-state equilibrium Si–H distance. Cade and Huo$^9$ in their pioneering ab initio work reported Hartree–Fock–Fock calculations on the ground state of Si–H as well as spectroscopic constants and made thorough comparisons with other second-row diatomic hydrides. Correlated wave functions obtained through the CEPA (coupled electron pair) method were used for the study of the ground state of the first- and second-row hydrides by Meyer and Rosmus.$^{10}$ Although they used rather extended basis sets for all molecules studied, and their results are in fair agreement with experimental numbers, it should be remembered that the CEPA approach does not lead to variational wave functions. Also, Goddard and Harding$^{11}$ in their description of chemical bonding in second-row hydrides refer to Si–H in different electronic states, but they do not give quantitative results. While both experiments$^{7-13}$ and theory$^{8-12,14}$ identify the ground state of Si–H as $^\text{II}$, the $^\Sigma^+$ has not been observed experimentally. This is apparently due to the difference in multiplicity from other low-lying states rendering a transition forbidden or very weak.

As far as we know no theoretical work, ab initio or semiempirical, has ever been published on lithiated-silicon molecular systems, in sharp contrast with carbon-lithiated species.$^{15}$ Si–Li vapors have been observed in the blasting of granite specimens with powerful laser beams,$^{16}$ but, other than experiments of this type, experimental work with the purpose of understanding the chemistry and/or physics of isolated silicon–lithium systems is to the best of our knowledge nonexistent.

In what follows we present ab initio quantum-mechanical calculations for the molecules Si–H, Si–Li, and C–Li in their ground and first low-lying states. Our intent is to delineate the differences and/or similarities between Si–H and Si–Li, as well as to compare them with the analogous species C–H and C–Li. Potential curves are generated for a significant range of internuclear distances for all three molecules in the $^\text{II}$ and $^\Sigma^-$ states, and equilibrium geometries ($R_e$), dissociation energies ($D_e$), and spectroscopic constants are determined. For the C–H molecule we refer to the accurate work by Lie and Hinze.$^5$

**Basis Sets and Molecular Codes**

Gaussian basis sets were obtained from Huzinaga's compilation$^{17}$ and used for the molecules Si–H and Si–Li. In particular the (11s,7p) for Si, (4s) for H, and (9s) for Li were augmented by polarization functions (two d components$^{18}$ on Si, two p functions$^{19}$ on H, and four p components$^{20}$ on Li) and contracted according to Raffenetti$^{20}$ to [3s,3p,1d] on Si, [3s,1p] on H, and [3s,1p] on Li. The d functions on Si in Si–H, as well as the (d,p) functions on Si and Li in Si–Li, were scaled to 1.50, 0.90, and 1.20, respectively. The scale factors were optimized at the SCF level in the corresponding ground states and used for all states and internuclear separations.

For C–Li the Duijneveldt$^{21}$ Gaussian basis (11s,8p/11s) was used; it was augmented by a single set of d polarization functions on C and four p functions on Li,$^{19}$ and it was contracted$^{20}$ to [3s,3p,1d]/3s,1p]. The exponent of the d functions as well as the scale factor for the lithium p orbitals were optimized at the SCF level in the $^\Sigma^+$ state of C-Li$_2$ and are reported elsewhere.$^5$

All calculations were carried out at Argonne National Laboratory using the collection of codes maintained by the Theoretical Chemistry Group. The integral evaluation and transformations were carried out with the programs BIGMOLI$^{22}$ and TRAOMO written by R. C. Raffenetti. The GVB wave functions were constructed with the program GVBTWO, originally written by F. Bobrowicz and W. Wadt with later modifications by L. G. Yaffe, A. K. Rappe, and others. The configuration lists for the CI calculations were generated by the program CIGEN written by B. D. Olafson and R. C. Ladmir with modifications by L. B. Harding. The CI calculations were carried out by using the program CITWO written by F. Bobrowicz with extensive modifications by S. P. Walch. A large part of our calculations, in particular those referring to $^\Sigma^-$ states, were done by using the program ALIS.$^{23}$ The contour plots were generated by using a version of CALTECH program CONTURM as modified by S. P. Walch and R. C. Raffenetti to make use of the general contraction scheme. Equilibrium geometries and spectroscopic constants were calculated by employing the program VIBROTIN written by T. H. Dunning, Jr.

**Computational Details**

The HF wave functions for Si–H and Si–Li can be written as

\[
\begin{align*}
\ket{^\text{II}} &= A_1 \sigma^2 \sigma^3 \sigma^2 4 \sigma^5 5^2 \pi^1 (2\pi^1_1 \alpha) \\
\ket{^\Sigma^+} &= A_1 \sigma^2 \sigma^3 \sigma^4 \sigma^2 1^2 \pi^1 (5\sigma^2_1 \pi^1_1 \alpha \alpha \alpha)
\end{align*}
\]

Si–Li

\[
\begin{align*}
\ket{^\text{II}} &= A_1 \sigma^2 \sigma^3 \sigma^2 4 \sigma^5 6^2 \pi^4 (2\pi^1_1 \alpha) \\
\ket{^\Sigma^+} &= A_1 \sigma^2 \sigma^3 \sigma^2 4 \sigma^5 6^2 \pi^4 (6\sigma^2_1 \pi^1_1 \alpha \alpha \alpha
\end{align*}
\]
Electrons in the orbitals 1σ, 2σ, 3σ, 1π, and 1σ, 2σ, 3σ, 4σ, 1π for Si–H and Si–Li, respectively, are well localized at the atomic centers and will be called "(core)". We are left with five "active" electrons which are the only ones to be considered in all correlated calculations; the rest are maintained doubly occupied.

In addition to these restricted SCF functions, we constructed small MCSCF functions for the 2π and 1Σ states. The configurations used permit the molecules to separate into the appropriate ground-state atoms and account for the near-degeneracy effect of Si 3s and 3p orbitals.

The configurations used for the 1Σ state of Si–H are

\[
\begin{align*}
(\text{core})4\sigma^25\sigma^22\pi_x & \quad (\text{core})2\pi_x^25\sigma^22\pi_x \\
(\text{core})4\sigma^26\sigma^22\pi_x & \quad (\text{core})2\pi_x^26\sigma^22\pi_x \\
(\text{core})4\sigma^25\sigma6\sigma2\pi_x & \quad (\text{core})2\pi_x^25\sigma6\sigma2\pi_x
\end{align*}
\]

The physical interpretation of these orbitals is clearest when the internuclear separation is very large. Here the 4σ and 2σ become the 3s and 3p on Si while the combinations 5σ ± 6σ become the 3p, and H's orbitals; as R is decreased, the 4σ, 2σx, and 2σy change little while the 5σ evolves into the major contributor to the chemical bond. In the GVB picture the combination 4σ ± λ2π is the lobes, l4, and the combination 5σ ± μσ are the approximate bonding orbitals. Schematically we have

\[\text{Si}^+(\text{P}) + \text{H}^+(\text{S}) \rightarrow \text{Si–H}^{2\Sigma^+}\]

or

\[\text{Si}^+(\text{P}) + \text{H}^+(\text{S}) \rightarrow \text{Si–H}^{(\text{II})}\]

The configurations used for the 1Σ state of Si–H are

\[
\begin{align*}
(\text{core})4\sigma^25\sigma2\pi_x2\pi_x & \\
(\text{core})6\sigma5\sigma2\pi_x2\pi_x & \\
(\text{core})4\sigma6\sigma5\sigma2\pi_x2\pi_x
\end{align*}
\]

At large R the 4σ and 6σ are the 3s and 3p orbitals of Si while the 5σ is the H's orbital. The 2σx and 2σy are the Si 3p and 3p orbitals, respectively. Note that at large R the GVB l4 orbitals are the 4σ ± 6σ combinations and are puffed along the incipient internuclear line. The 4σ + 6σ combination (l4) is puffed toward the incoming H while the 4σ − 6σ combination (l4) is puffed in the opposite direction. As R is decreased, the role played by these orbitals undergoes a significant change. In particular the in-phase combination of 4σ and 6σ (l4) becomes silicon's contribution to the chemical bond, while the out-of-phase 4σ and 6σ (l4) contribution evolves into a hydrogen contribution. Concurrently, the 5σ changes from H's to l4, i.e., 3s − 3p. Schematically we have

\[\text{Si}^+(\text{P}) + \text{H}^+(\text{S}) \rightarrow \text{Si–H}^{2\Sigma^+}\]

Since the above discussion is qualitatively identical for Si–Li (and C–Li), it need not be repeated. We collect in Figures 6, 7, 9, and 10 the contours of the orbitals hosting the five active electrons in each of the 2Σ and 1Σ states for both Si–H and Si–Li systems. Note that the MCSCF calculations for the 2Π states were done with the computer code SOGVB while those for the 1Σ were done with the ALIS program.

**POL-Cl and MCSCF + 1+2 Wave Functions**

In the polarization CI (POL-Cl) wave function all single and double excitations are generated relative to the MCSCF configurations (six and three for the 2Π and 1Σ states, respectively, in the present study) subject to the restriction that no more than one electron occupy an orbital outside the valence orbitals. In the MCSCF+1+2 CI all singles and doubles are considered from the reference configurations with no restrictions. We emphasize that, while all electrons are explicitly included in the CI, only five electrons are correlated.

**Results**

Tables I–III give absolute energies, equilibrium bond distances, and spectroscopic constants for the molecules Si–H, Si–Li, and C–Li, respectively, in the two states.
TABLE II: Energies ($E$), Equilibrium Bond Lengths ($R_e$), Dissociation Energies ($D_e$), Force Constants ($k_f$), and Spectroscopic Constants of Si-Li in the $X^4\Sigma^-$ and $a^2\Pi$ States

<table>
<thead>
<tr>
<th>method</th>
<th>$E$, hartree</th>
<th>$\Delta E_Q$, hartree</th>
<th>$R_e$, bohr</th>
<th>$D_e$, kcal mol$^{-1}$</th>
<th>$10^{-1}k_f$, dyn cm$^{-1}$</th>
<th>$\omega_e$, cm$^{-1}$</th>
<th>$\omega_e\chi_e$, cm$^{-1}$</th>
<th>$R_e$, cm$^{-1}$</th>
<th>$\alpha_e$, cm$^{-1}$</th>
<th>$10^4D_e$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X^4\Sigma^-$ State</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF</td>
<td>-296.30868</td>
<td>-0.0045</td>
<td>4.595</td>
<td>13.9</td>
<td>0.659</td>
<td>446.7</td>
<td>3.65</td>
<td>0.5082</td>
<td>0.0054</td>
<td>0.0</td>
</tr>
<tr>
<td>SCF+1+2</td>
<td>-296.37283</td>
<td>-0.0078</td>
<td>4.658</td>
<td>13.9</td>
<td>0.627</td>
<td>435.5</td>
<td>3.88</td>
<td>0.4946</td>
<td>0.0049</td>
<td>0.0</td>
</tr>
<tr>
<td>ALIS</td>
<td>-296.31735</td>
<td></td>
<td>4.631</td>
<td>25.9</td>
<td>0.630</td>
<td>436.5</td>
<td>3.00</td>
<td>0.5003</td>
<td>0.0052</td>
<td>0.0</td>
</tr>
<tr>
<td>POL-CI</td>
<td>-296.35052</td>
<td></td>
<td>4.674</td>
<td>28.8</td>
<td>0.602</td>
<td>426.7</td>
<td>3.81</td>
<td>0.4912</td>
<td>0.0053</td>
<td>0.0</td>
</tr>
<tr>
<td>ALIS+1+2</td>
<td>-296.37373</td>
<td></td>
<td>4.664</td>
<td>35.2</td>
<td>0.609</td>
<td>429.4</td>
<td>2.78</td>
<td>0.4934</td>
<td>0.0050</td>
<td>0.0</td>
</tr>
<tr>
<td>$a^2\Pi$ State</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF</td>
<td>-296.26989</td>
<td></td>
<td>4.955</td>
<td>4.7</td>
<td>0.554</td>
<td>409.5</td>
<td>2.45</td>
<td>0.4371</td>
<td>0.0040</td>
<td>0.0</td>
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<td>SCF+1+2</td>
<td>-296.34648</td>
<td></td>
<td>5.034</td>
<td>5.0</td>
<td>0.468</td>
<td>376.1</td>
<td>2.84</td>
<td>0.4236</td>
<td>0.0046</td>
<td>0.0</td>
</tr>
<tr>
<td>MCSCF</td>
<td>-296.29361</td>
<td></td>
<td>5.223</td>
<td>11.3</td>
<td>0.277</td>
<td>259.5</td>
<td>3.05</td>
<td>0.3933</td>
<td>0.0058</td>
<td>0.0</td>
</tr>
<tr>
<td>POL-CI</td>
<td>-296.32986</td>
<td></td>
<td>5.153</td>
<td>16.0</td>
<td>0.133</td>
<td>394.1</td>
<td>14.77</td>
<td>0.4042</td>
<td>0.0069</td>
<td>0.0</td>
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<tr>
<td>MCSCF+1+2</td>
<td>-296.35062</td>
<td></td>
<td>5.075</td>
<td>20.7</td>
<td>0.438</td>
<td>363.9</td>
<td>4.65</td>
<td>0.4166</td>
<td>0.0053</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$\Delta E_Q$ is the Davidson correction$^{26}$ for unlinked clusters (simultaneous pair correlations) given by

$$\Delta E_Q = (1 - C_0^2)\Delta E_{SD}$$

where $C_0$ is the coefficient of the SCF wave function in the CI (SCF+1+2) expansion and $\Delta E_{SD}$ is the correlation energy gained due to single and double excitations. Figures 1–3 present potential energy curves for the three molecules in the two states, and a comparison is made among the different levels of computation used. We note that, although the POL-CI does fairly well for the systems studied here, qualitative results of the same validity can be obtained by a small MCSCF expansion of the appropriate form.

For the Si–H species the ground state is clearly a $^2\Pi$ state with a calculated binding energy of 65.7 kcal mol$^{-1}$ at the MCSCF+1+2 level. This is in good agreement with the experimental value of less than 70.6 kcal mol$^{-1}$ given in the Huber–Herzberg$^4$ compilation. A more recent, and apparently much more accurate, determination of dissociation$^{27}$ energy of Si–H gives a value of 77.06 ± 0.6 kcal


Electronic Structure of C-Li, Si-H, and Si-Li


Figure 3. C-Li potential energy curves.

Figure 4. Calculated bonding energy of C-H, C-Li, Si-H, and Si-Li.

Table IV: $E(\Sigma^+)-E(\Pi)$ Energy Separations (kcal mol$^{-1}$)

<table>
<thead>
<tr>
<th>Method</th>
<th>Si-H</th>
<th>Si-Li</th>
<th>C-Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF + 1 + 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF + 1 + 2 + $\Delta E_Q$</td>
<td>-34.6</td>
<td>16.5</td>
<td>37.2</td>
</tr>
<tr>
<td>MCSCF + 1 + 2 + ALIS + 1 + 2</td>
<td>-36.0</td>
<td>14.5</td>
<td>34.2</td>
</tr>
<tr>
<td></td>
<td>-36.1</td>
<td>14.5</td>
<td>33.3</td>
</tr>
</tbody>
</table>

* Reference 3.

Figure 5. Comparison of Si-H and C-H potential energy curves. The Si-H curves have been shifted downward to permit a direct comparison between the $^2\Pi$ vibrational levels.

Figure 6. Valence orbital contours of Si-H at the equilibrium separation in the $^2\Pi$ state. The plots have uniformly spaced contours with increments of 0.05 au. Positive contours are indicated by solid lines, negative contours are indicated by dotted lines, and nodal planes by long dashes. The same conventions are used for all plots.

Table IV: $E(\Pi^+)-E(\Pi^-)$ Energy Separations (kcal mol$^{-1}$)

<table>
<thead>
<tr>
<th>Method</th>
<th>Si-H</th>
<th>Si-Li</th>
<th>C-Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF + 1 + 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCF + 1 + 2 + $\Delta E_Q$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCSCF + 1 + 2 + ALIS + 1 + 2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Taking the latter determination of $D_0$ as more realistic, we believe that a large component of the 11 kcal mol$^{-1}$ differential between the calculated and experimental value is due to the limitations in our basis set, in particular its polarization space. The experimental spectroscopic constants of Si-H in the $^3\Pi$ state (Table I) agree fairly well with the calculated values at the MCSCF + 1 + 2 level. It is interesting to note the excellent agreement between the experimental bond length and dissociation energy and the corresponding SCF values.

The MCSCF + 1 + 2 + ALIS + 1 + 2 (or SCF + 1 + 2 + $\Delta E_Q$) calculations locate the $^4\Sigma^+$ state 36 kcal mol$^{-1}$ above the $^3\Pi$ state, with a dissociation energy of 29.7 kcal mol$^{-1}$ with respect to ground-state atoms (Tables I and IV, Figure 1). The analogous numbers for C-H obtained by Lie and Hinze$^a$ are 15.5 and 65.4 kcal mol$^{-1}$ respectively (Figure 4). Figure 5 compares the potential energy curves

and vibrational levels of Si-H and C-H molecules in the $^3\Pi$ and $^4\Sigma^+$ states. It should be noted that the zeroth level of the Si-H $^2\Pi$ curve has been shifted to make the comparison easier (see also ref 27).

Figures 6 and 7 show the valence GVB (nonorthogonal) orbitals of Si-H in the states $^3\Pi$ and $^4\Sigma^+$, respectively. In the state $^3\Pi$ (Figure 6) we observe the bending back of the two lobes due to repulsive interactions with the valence bond orbitals. The bond formation is clearly depicted in the "bond" orbitals suggesting a deformation of the $p_x$ Si orbital and a transferring of charge from the silicon to hydrogen atom. The $p_x$ of Si remains practically unaf-
The ‘Σ’ state of Si–H obtains when the hydrogen bonds to a lobe requiring the uncoupling of the singlet coupled lobe pair. This lobe breaking is largely responsible for the

\[ 1Σ \] state being higher than the \( ^2Π \) state.\(^\text{12}\) The same situation prevails for the C–H molecule, yet for the latter the \( ^4Σ^- \) state is \( \sim 20 \text{ kcal mol}^{-1} \) lower\(^3\) than in the Si–H species (Figure 4). In Figure 7 the valence orbitals of Si–H in \( ^4Σ^- \) are plotted. The picture of the bond orbitals again suggests a charge transfer from Si to H, and that the \( p_x \) and \( p_y \) orbitals of the Si are only slightly influenced by the bond formation.

Consider now the molecule Si–Li. The two states examined, the \( ^2Π \) and the \( ^4Σ^- \), are obtained formally in the same way as in the Si–H system. The \( 1s^2 \) electrons of the Li atom do not participate in the bond formation, so we

---

are dealing again with a "one-electron system" interacting with the Si atom. Table II presents absolute energies, equilibrium bond lengths, dissociation energies, and spectroscopic constants for both states. Figure 2 shows a series of potential curves and Figure 8 compares the potential curves and vibrational levels of Si-Li and C-Li at the MCSCF+1+2/ALIS+1+2 level.

Note that both the \(4\Sigma^+\) and \(^3\Sigma^+\) states are bound (by 35 and 21 kcal mol\(^{-1}\), respectively) and the \(^2\Sigma^+\) is the ground state. Contours of the valence orbitals of Si-Li are shown in Figures 9 and 10 and are remarkably similar to the corresponding C-Li plots. In particular, the \(4\Sigma^+\) contours indicate that the singlet coupled pair which in Si-H is a bond is a doubly occupied 3s orbital on Si in Si-Li. Further, while the L orbital in Si-H is a "lobe", in Si-Li it is essentially a 3p, Si orbital. Similarly the contours for the \(^2\Pi\) state shown in Figure 10 suggest that the bond is dominated by the 3p\(_{\sigma}\) orbital and that the lobes, \(l_1\) and \(l_2\), show the effect of the interaction with Li, being bent away from the bond. Note that they are considerably less "bent" than in the \(^2\Pi\) state of C-Li primarily because the Si-Li bond length is so much larger (5.075 vs. 4.026 au).

In summary, while C-H and Si-H have \(^2\Pi\) ground states, both C-Li and Si-Li have \(^4\Sigma^+\) ground states. This interesting feature suggests that the reactions in which two C-Li or Si-Li fragments couple, i.e.

\[
\text{C-Li} + \text{C-Li} \rightarrow \text{Li} = \text{C} = \text{C-Li}
\]

would proceed along the least-motion path with no activation energy. This is to be contrasted with the C-H situation where the least-motion pathway is characterized by a barrier estimated\(^{29}\) at 12 kcal mol\(^{-1}\). We suspect that the plethora of unconventional structures of organic molecules which are predicted to arise when one or more hydrogens are replaced by Li may be traced to the preference of C-Li for a \(^2\Sigma^+\) ground state. If so, the various mixed compounds of silicon, carbon, and lithium would seem to be a fruitful area for theoretical study. We are pursuing these ideas.

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