

Figure 3. C-Li potential energy curves.

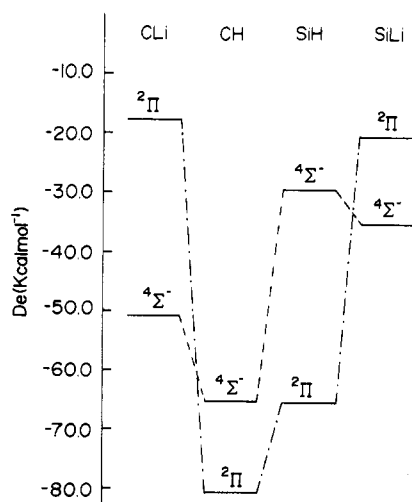


Figure 4. Calculated bonding energy of C-H, C-Li, Si-H, and Si-Li.

TABLE IV:  $E(^2\Pi) - E(^4\Sigma^-)$  Energy Separations ( $\text{kcal mol}^{-1}$ )

| method                | $\Delta E(^2\Pi) - ^4\Sigma^-$ |       |                   |
|-----------------------|--------------------------------|-------|-------------------|
|                       | Si-H                           | Si-Li | C-Li              |
| SCF+1+2               | -34.6                          | 16.5  | 37.2              |
| SCF+1+2+ $\Delta E_Q$ | -36.0                          | 14.5  | 34.2 <sup>a</sup> |
| MCSCF+1+2/ALIS+1+2    | -36.1                          | 14.5  | 33.3              |

<sup>a</sup> Reference 3.

$\text{mol}^{-1}$ ; taking the latter determination of  $D_0$  as more realistic, we believe that a large component of the 11  $\text{kcal mol}^{-1}$  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  $X^2\Pi$  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  $\text{kcal mol}^{-1}$  above the  $X^2\Pi$  state, with a dissociation energy of 29.7  $\text{kcal mol}^{-1}$  with respect to ground-state atoms (Tables I and IV, Figure 1). The analogous numbers for C-H obtained by Lie and Hinze<sup>5</sup> are 15.5 and 65.4  $\text{kcal mol}^{-1}$  respectively (Figure 4). Figure 5 compares the potential energy curves

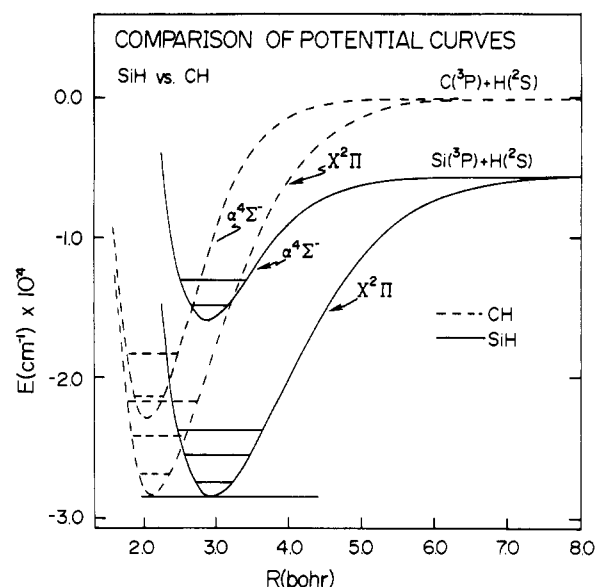


Figure 5. Comparison of Si-H and C-H potential energy curves. The Si-H curves have been shifted downward to permit a direct comparison between the  $^2\Pi$  vibrational levels.

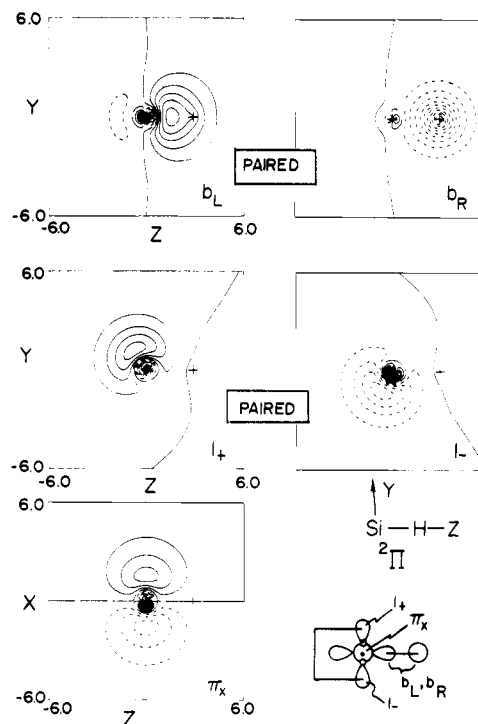
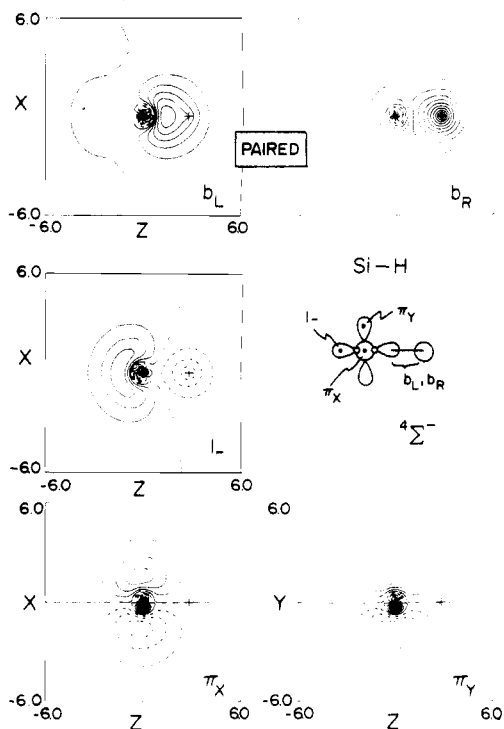


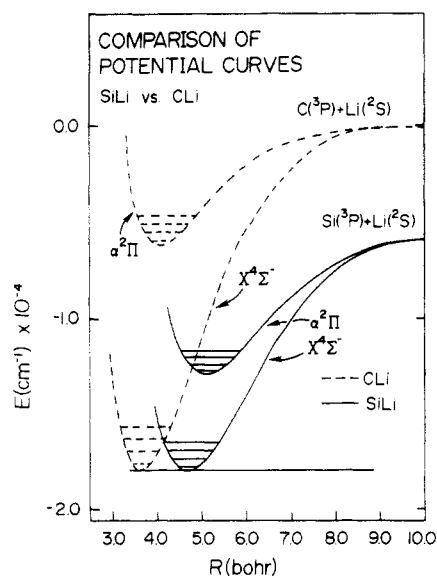
Figure 6. Valence orbital contours of Si-H at the equilibrium separation in the  $^2\Pi$  state. The plots have uniformly spaced contours with increments of 0.05 au. Positive contours are indicated by solid lines, negative contours are indicated by dotted lines, and nodal planes by long dashes. The same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

and vibrational levels of Si-H and C-H molecules in the  $^2\Pi$  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  $^2\Pi$  and  $^4\Sigma^-$ , respectively. In the state  $^2\Pi$  (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  $p_z$  Si orbital and a transferring of charge from the silicon to hydrogen atom. The  $p_x$  of Si remains practically unaf-

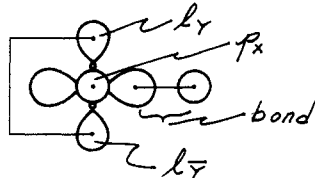


**Figure 7.** Valence orbital contours of Si-H at the equilibrium separation in the  $4\Sigma^-$  state.



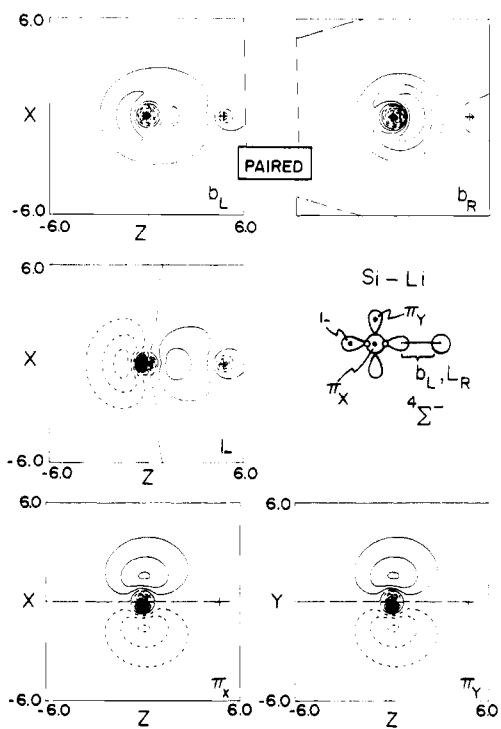
**Figure 8.** Comparison of Si-Li and C-Li potential energy curves. The Si-Li curves have been shifted downward to permit a direct comparison between the  $4\Sigma^+$  vibrational levels.

ected from the bond formation. The above discussion can be summarized in the GVB picture (see also ref 28).

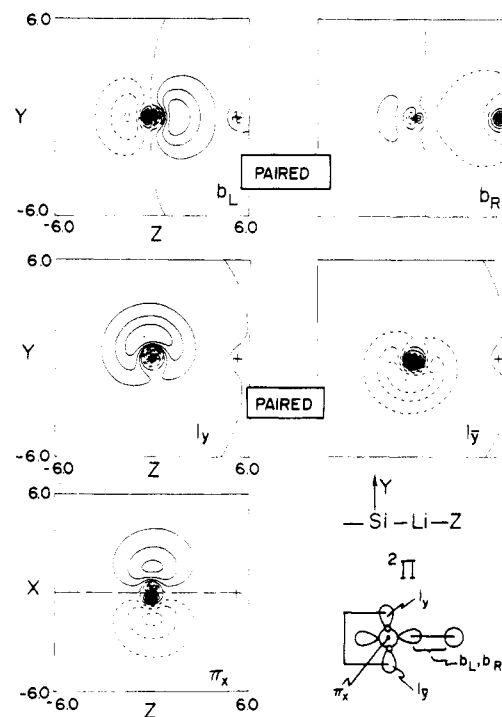


The  $4\Sigma^-$  state of Si-H obtains when the hydrogen bonds to a lobe requiring the uncoupling of the singlet coupled lobe pair. This lobe breaking is largely responsible for the

(28) W. A. Goddard, III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, 6, 368 (1973).



**Figure 9.** Valence orbital contours of Si-Li at the equilibrium separation in the  $4\Sigma^+$  state.



**Figure 10.** Valence orbital contours of Si-Li at the equilibrium separation in the  $2\Pi$  state.

$4\Sigma^-$  state being higher than the  $2\Pi$  state.<sup>12</sup> The same situation prevails for the C-H molecule, yet for the latter the  $4\Sigma^-$  state is  $\sim 20$  kcal mol<sup>-1</sup> lower<sup>3</sup> than in the Si-H species (Figure 4). In Figure 7 the valence orbitals of Si-H in  $4\Sigma^-$  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.

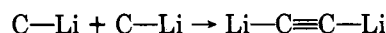
Consider now the molecule Si-Li. The two states examined, the  $2\Pi$  and the  $4\Sigma^+$ , are obtained formally in the same way as in the Si-H system. The  $1s^2$  electrons of the Li atom do not participate in the bond formation, so we

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  $^2\Pi$  states are bound (by 35 and 21 kcal mol<sup>-1</sup>, respectively) and the  $^4\Sigma^-$  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<sub>z</sub> Si orbital. Similarly the contours for the  $^2\Pi$  state shown in Figure 10 suggest that the bond is dominated by the 3p<sub>z</sub> orbital and that the lobes, l<sub>y</sub> and l<sub>x</sub>, 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 inter-

esting feature suggests that the reactions in which two C-Li or Si-Li fragments couple, i.e.



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<sup>29</sup> at 12 kcal mol<sup>-1</sup>. 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  $^4\Sigma^-$  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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## Effect of Electron Scavengers To Reduce the Ionization Current of Photoexcited *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine in Nonpolar Organic Liquids

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The effects of perfluoro-*n*-hexane, perfluoro-*n*-heptane, perfluoromethylcyclohexane, and perfluorodecalin to reduce the ionization current of photoexcited *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) have been studied in the solvents tetramethylsilane, 2,2-dimethylbutane (2,2-DMB), isooctane, cyclohexane, *n*-hexane, and *n*-pentane. Results are reported over a range of excitation energies from 5.2 to 6.7 eV and, for selected systems, over a temperature range from -78 to 25 °C. At quencher concentrations,  $c_q \leq 0.2$  M, the ratio of the photocurrent without quencher,  $J_0$ , to that with quencher,  $J$ , is found to be concave upward, linear, or concave downward in its dependence on  $c_q$ , depending on the system studied. At higher  $c_q$ ,  $J_0/J$  is always concave upward. Both  $J_0$  and  $J$  increase to about the same extent as the excitation energy increases, thus maintaining  $J_0/J$  constant. As the temperature increases,  $J$  increases somewhat more rapidly than does  $J_0$  and increasingly so the larger is  $c_q$ . An attempt is made to explain these results with a model based on interaction of the quencher with an epithermal electron.

### Introduction

All observations that have so far been made on the photoionization of TMPD in neat nonpolar liquids are consistent with the following view of the process. At the photoionization threshold there is generated a quasi-free electron which thermalizes at some distance from its sibling positive ion. This geminate pair then move stochastically in their mutual Coulomb field, either escaping each other, with low probability (to generate a photocurrent in the presence of a small external field), or, with much larger probability, recombining, without significant loss of spin polarization, to generate the fluorescing state of TMPD. The evidence for all of this is obtained from (i) the solvent dependence of the photocurrent energy threshold (which supports the quasi-free nature of the ejected electron),<sup>1,2</sup>

(ii) the external field dependence of the photocurrent (which supports the stochastic nature of the motion of the geminate pair),<sup>1-4</sup> and (iii) the dependence of the fluorescence quantum yield on both excitation energy<sup>5</sup> and applied field strength<sup>6,7</sup> (which support the retention of

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