

# Laser photoelectron spectrometry of the negative ions of silicon and its hydrides\*

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Fixed-frequency laser photoelectron spectrometry has been utilized to study the ions  $\text{Si}^-$ ,  $\text{SiH}^-$ , and  $\text{SiH}_2^-$ . In each case, the photodetached electron energy spectrum consists primarily of sharp, easily assignable peaks. The electron affinities of Si, SiH, and  $\text{SiH}_2$  have been determined to be  $(1.385 \pm 0.005)$  eV,  $(1.277 \pm 0.009)$  eV, and  $(1.124 \pm 0.020)$  eV, respectively. Two bound excited states attributed to  $^2D$  and  $^2P$  terms have been observed for  $\text{Si}^-$ , and their binding energies determined. Similarly, two bound excited states, assigned to  $^1A$  and  $^1\Sigma^+$  symmetry, have been discovered in  $\text{SiH}^-$ . The internuclear distance  $r_e$  in the ground state of  $\text{SiH}^-$  has been determined by a Franck-Condon factor analysis to be  $(1.474 \pm 0.004)$  Å. In addition, spectroscopic constants of the excited states have been deduced. Transitions from the ground state of  $\text{SiH}^-$  to both the  $^1A_1$  and  $^3B_1$  states of  $\text{SiH}_2$  have been observed; unlike the case of  $\text{CH}_2$ , the  $^1A_1$  state is the lower in energy.

## I. INTRODUCTION

Fixed-frequency laser photoelectron spectrometry of negative ions has recently been utilized to determine the electron affinities (EA) of a variety of atomic and molecular species to a high degree of accuracy.<sup>1-5</sup> This paper reports the use of this technique to study  $\text{Si}^-$ ,  $\text{SiH}^-$ , and  $\text{SiH}_2^-$  in order to determine the EA's of the corresponding neutral species and to ascertain the energies of any bound excited states of the negative ions.

The ground electronic configuration of  $\text{Si}^-$ ,  $1s^2 2s^2 2p^6 3s^2 3p^3$ , gives rise to terms of  $^4S$ ,  $^2D$ , and  $^2P$  symmetries. There is both experimental and theoretical evidence that all three of these states are bound with respect to the ground  $^3P$  state of Si.<sup>6-10</sup> Hartree-Fock calculations by Clementi *et al.*<sup>6</sup> and model potential calculations by Hunt and Moiseiwitsch<sup>10</sup> show that the energy ordering of the three  $\text{Si}^-$  states is that predicted by Hund's rules:  $^4S < ^2D < ^2P$ . The binding energy of the ground  $^4S$  state (the Si electron affinity) has been studied by a variety of methods.<sup>6,7,10-14</sup> Model potential calculations by Hunt and Moiseiwitsch<sup>10</sup> yield an affinity of 1.41 eV, whereas Hartree-Fock calculations by Clementi *et al.*,<sup>6</sup> corrected empirically for correlation effects, give a value of 1.39 eV. Extrapolation techniques ("horizontal analyses") have been applied by a number of investigators who have obtained affinities ranging from 1.36–1.46 eV.<sup>11-14</sup> Feldmann<sup>7</sup> has studied the total photodetachment cross section of  $\text{Si}^-$  as a function of wavelength. His results, which are difficult to interpret because of the overlapping of several photodetachment onsets, yield an affinity of  $\sim 1.40$  eV.

The Hartree-Fock calculation by Clementi *et al.*<sup>6</sup> of the two low-lying excited states of  $\text{Si}^-$  shows the  $^2D$  state to be bound [relative to  $\text{Si}(^3P)$ ] by 0.58 eV and the  $^2P$  state by 0.08 eV. The model potential values are 0.59 eV and 0.065 eV, respectively.<sup>10</sup> Feldmann's<sup>7</sup> photode-

tachment study provides a value of  $(0.56 \pm 0.04)$  eV for the  $^2D$  binding energy. Il'in and co-workers<sup>8,9</sup> have utilized field-induced ionization of  $\text{Si}^-(^2P)$  to determine a value of 0.037 eV for the binding energy of this state. Because a substantial theoretical formalism is required to derive the binding energy from the data, it is difficult to obtain quantitative error limits for their result.

The silicon monohydride ion,  $\text{SiH}^-$ , has a ground  $\sigma^2 \pi^2$  configuration which gives rise to states of  $^3\Sigma^-$ ,  $^1\Delta$ , and  $^1\Sigma^+$  symmetries. In the analogous NH and PH molecules, the energy ordering of these states is  $X^3\Sigma^- < a^1\Delta < b^1\Sigma^+$ .<sup>15-18</sup> Our results indicate that all three of these states in  $\text{SiH}^-$  have potential minima below that of  $X^2\Pi$   $\text{SiH}$ . In addition, the three bound states of  $\text{SiH}^-$ , assumed to have the same energy ordering as NH and PH, dissociate to the three bound states of  $\text{Si}^-$  and  $\text{H}(1s^2S)$ . Our value for the affinity of  $\text{SiH}$  is remarkably similar to the value for free silicon.

The electron affinity of  $\text{SiH}_2$  has been indirectly estimated by Gaines and Page<sup>19</sup> to be  $\sim 3.47$  eV, much higher than the present result. From the ground ( $^2B_1$ ) state of  $\text{SiH}_2^-$ , we observe transitions to both the  $^1A_1$  and  $^3B_1$  states of  $\text{SiH}_2$ . The energy spacing between these two states in the analogous  $\text{CH}_2$  molecule has long been a matter of controversy<sup>20</sup>; calculations of this energy difference for  $\text{SiH}_2$  by Wirsam<sup>21</sup> place the  $^1A_1$  state below the  $^3B_1$  state, in contrast to the  $\text{CH}_2$  result. In addition to the photodetachment studies of the silicon hydrides presented in this paper, Reed and Brauman have recently obtained relative photodetachment cross sections for  $\text{SiH}_3^-$ ,<sup>22</sup> utilizing an ICR apparatus to photodetach trapped  $\text{SiH}_3^-$  ions.

## II. TECHNIQUE

### A. Apparatus

The apparatus and experimental techniques used in this work have been described previously in detail.<sup>1</sup> Beams

of  $\text{Si}^-$ ,  $\text{SiH}^-$ , and  $\text{SiH}_2^-$  are produced in a low pressure discharge source upon admission of silane ( $\text{SiH}_4$ ). The ion beams are accelerated to 680 eV and mass analyzed by a Wien filter. Upon entering the interaction region, depicted in Fig. 1, the ions are crossed with the focused, intracavity beam of a continuous argon-ion laser operating at  $4880 \text{ \AA}$  ( $h\nu = 2.540 \text{ eV}$ ). Typical beam currents collected by the Faraday cup behind the interaction region are 0.3–1.0 nA. Those photodetached electrons that enter the acceptance angle of the hemispherical electrostatic monochromator are energy analyzed and then detected by a particle multiplier. The monochromator has a resolution of 50 meV (FWHM) and operates at a fixed transmission energy. The complete (0–2.54 eV) energy spectrum of the photodetached electrons is obtained by digital accumulation using a multichannel analyzer.

### B. Data analysis

The spectra measured in this experiment correspond to dipole-allowed detachment transitions between electronic states (both ground and excited) of the negative ions and such states of the neutral species. The spectra are measured as a function of the energy of the detached electrons. The peaks are fitted to asymmetric Gaussian line shapes<sup>1</sup> enabling the peak centers to be determined to  $\sim 1 \text{ meV}$ . Linewidths of the detachment transitions observed are  $\sim 50 \text{ meV}$  for  $\text{Si}^-$  (the resolution limit of the electron energy analyzer) and  $\sim 70 \text{ meV}$  for  $\text{SiH}^-$  and  $\text{SiH}_2^-$ , where the additional broadening is ascribed to rotational effects. By applying conservation of energy to the detachment process, one can show that the vertical detachment energy  $E$  of a transition is given by

$$E = h\nu - \Omega - \frac{mW}{M} + E_{cp}, \quad (1)$$

where  $h\nu$  is the incident photon energy (2.540 eV),  $\Omega$  is the laboratory energy of the photodetached electrons at the peak center,  $m/M$  is the ratio of electron to ion mass,  $W$  is the kinetic energy of the ion, and  $E_{cp}$  is the contact potential energy difference between the interaction region and the monochromator. (The third term is a kinematic correction which arises because those electrons which enter the analyzer were back scattered in the center-of-mass frame.) The detachment energy between the ground state of the ion and the ground state of the neutral corresponds to the electron affinity of the neutral species.

Since the contact potential  $E_{cp}$  is unknown and can vary over a short period of time, it is necessary to calibrate all energy measurements against a reference atom produced simultaneously in the ion source. Photoelectron spectra of the ion under consideration and a reference ion are accumulated simultaneously by switching the Wien filter back and forth between the two masses on a millisecond time scale. To calibrate the  $\text{Si}^-$  spectrum, the  $\text{K}^-$  ion was chosen (produced in our discharge source by vaporizing KBr) because the potassium affinity is well known ( $0.5012 \pm 0.0005 \text{ eV}$ ).<sup>23</sup> Unknown  $\text{Si}^-$  detachment energies are then determined in the following manner. First, the electron energy separation between the peak under consideration and the  $\text{K}(^2S) - \text{K}(^1S)$  peak is obtained. This energy separation,  $\Omega_{\text{K}} - \Omega_{\text{Si}^-}$ , is increased by a factor of 1.6% to compensate for the compression factor of our electron energy analyzer.<sup>24</sup> This compression factor has been described previously.<sup>4,5</sup> The  $\text{Si}^-$  detachment energies are given by the expression

$$E(\text{Si}^-) = EA(\text{K}) + 1.016(\Omega_{\text{K}} - \Omega_{\text{Si}^-}) + mW \left( \frac{1}{M_{\text{K}}} - \frac{1}{M_{\text{Si}^-}} \right). \quad (2)$$

Once the  $\text{Si}^-$  detachment energies and, in particular, the Si electron affinity are known, the photoelectron spectra

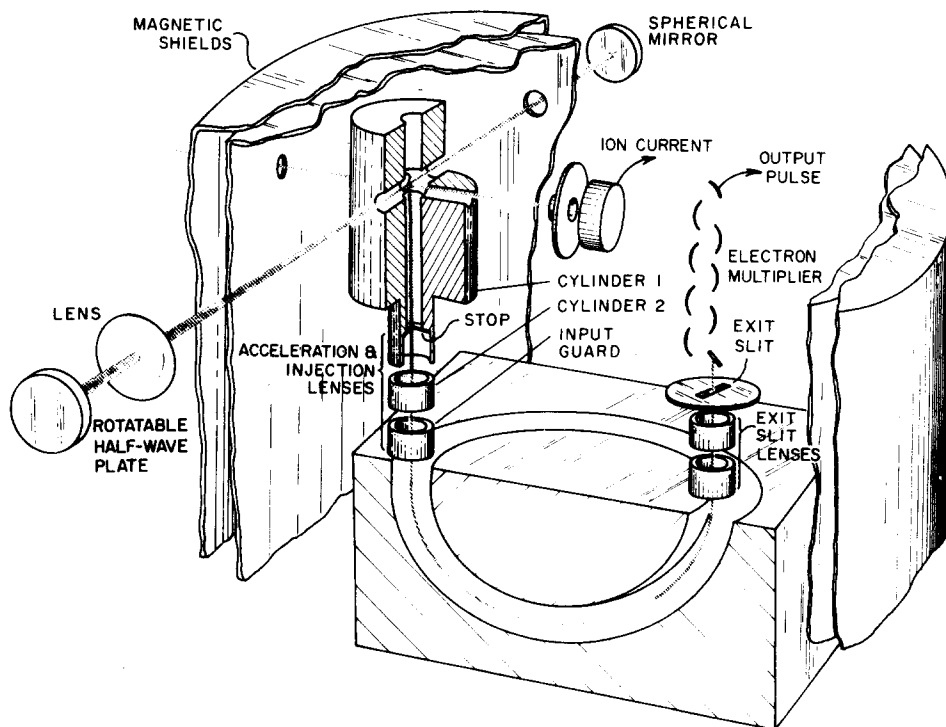


FIG. 1. A diagram of the interaction region and the electron energy analyzer.

of  $\text{SiH}^-$  and  $\text{SiH}_2^-$  are then calibrated against the measured Si affinity. Detachment energies calibrated against  $\text{K}^-$  or  $\text{Si}^-$  by the above method are obtained with an error of  $\pm(0.002 - 0.005)$  eV, depending upon the energy difference between the reference peak and the peak of interest.

### III. $\text{Si}^-$

The photoelectron spectrum of  $^{28}\text{Si}^-$  is depicted in Fig. 2. This spectrum, consisting of six discrete peaks, has been assigned to transitions between the three lowest states of  $\text{Si}^-(3p^3\ ^4S, \ ^2D, \ ^2P)$  and the three lowest states of  $\text{Si}(3p^2\ ^3P, \ ^1D, \ ^1S)$ .<sup>25</sup> The energy ordering of the  $3p^3$   $\text{Si}^-$  states is tentatively assumed to be  $^4S < ^2D < ^2P$ . In the observed photoelectron transitions, which obey one-electron dipole selection rules, one bound  $3p$  electron is detached into an  $s$  or  $d$  wave, and the resulting  $3p^2$  configuration of the remaining electrons determines the multiplet structure of the Si final state; viz.,

$$h\nu + \text{Si}^-(^4S) \rightarrow \text{Si}(^3P) + e$$

$$h\nu + \text{Si}^-(^2D) \rightarrow \text{Si}(^3P, \ ^1D, \ ^1S) + e$$

$$h\nu + \text{Si}^-(^2P) \rightarrow \text{Si}(^3P, \ ^1D, \ ^1S) + e$$

The photoelectron selection rule of  $\Delta S = \pm \frac{1}{2}$  is derived from conservation of total electronic spin. All allowed transitions are observed, with the exception of  $\text{Si}^-(^2D) \rightarrow \text{Si}(^4S)$ , which is energetically inaccessible. The particular assignments are supported by several arguments. One peak is by far the most intense; this peak and no other must involve the ground state of  $\text{Si}^-$ . Because  $\text{Si}^-(^4S)$  can only undergo one transition [to  $\text{Si}(^3P)$ ], this state is the negative ion ground state. In addition, transitions originating from different states of  $\text{Si}^-$  are altered in relative intensity when ion source conditions are changed. These and other considerations are not sufficient to determine the energy ordering of the excited  $^2D$  and  $^2P$   $\text{Si}^-$  states; this ordering ( $^2D < ^2P$ ) is chosen to agree with both that of phosphorous<sup>25</sup> and that of previous studies of  $\text{Si}^-$ .<sup>6-10</sup> Figure 3 shows the energy separa-

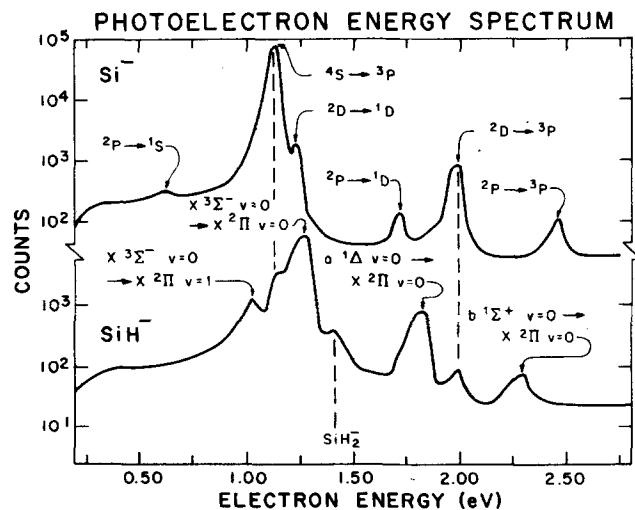


FIG. 2. Photoelectron spectra of  $\text{Si}^-$  and  $\text{SiH}^-$ . The logarithm of the number of electrons striking the detector is plotted against electron energy.

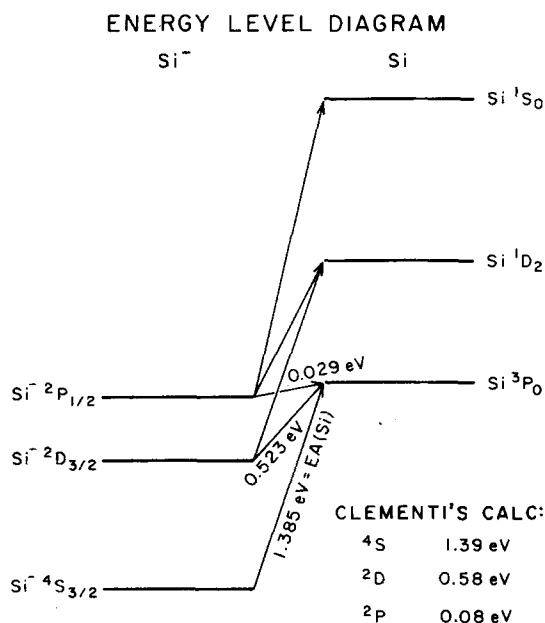


FIG. 3. The lowest energy levels of  $\text{Si}^-$  and Si with observed transitions. The reported  $\text{Si}^-$  binding energies have been corrected for spin-orbit effects. See text for further discussion.

tions among the observed states of  $\text{Si}^-$  and Si, along with measured transition energies. Since the  $^2D$  and  $^2P$  states of  $\text{Si}^-$  have the same  $3p^3$  electron configuration as the ground  $^4S$  state, all three states are of the same parity and both  $\text{Si}^-(^2D)$  and  $\text{Si}^-(^2P)$  are sufficiently metastable to survive the 30  $\mu\text{sec}$  flight time from ion source to interaction region.

The measured detachment (vertical) energies in our experiment do not resolve the spin-orbit splitting in  $\text{Si}^-(^2D, ^2P)$  and  $\text{Si}(^3P)$ . Rather, the vertical energies are admixtures of the various spin-orbit-split transitions and must be corrected to obtain the energy differences between the lowest fine structure levels. To do this, we assume that the statistical approximation holds,<sup>26</sup> i.e., that the transition strengths to the spin-orbit sublevels of  $\text{Si}(^3P)$  are in the ratio of the degeneracies of these levels ( $^3P_0 : ^3P_1 : ^3P_2 \rightarrow 1 : 3 : 5$ ). This conclusion is valid near threshold for the case when the fine structure levels in the initial (negative ion) state are not resolved and when Russell-Saunders coupling is obeyed. The detailed theory will be discussed in a forthcoming paper by Rau.<sup>27</sup> In any case, a breakdown of the statistical approximation will result in errors in the determined parameters of  $\leq 2$  meV; these errors are somewhat smaller than our experimental errors of  $\sim 5$  meV.

We also assume that the spin-orbit levels of  $\text{Si}^-(^2D)$  and  $\text{Si}^-(^2P)$  are populated according to their statistical weights. The spin-orbit separations in  $\text{Si}(^3P)$  are well known,<sup>25</sup> whereas those in  $\text{Si}^-(^2D, ^2P)$  are not. The latter are expected on theoretical grounds (half-filled shell) to be quite small ( $\ll 10$  meV), and an isoelectronic extrapolation<sup>25</sup> from PI, SII, and ClIII indicates that for  $\text{Si}^-$ ,  $\Delta(^2D_{5/2} - ^2D_{3/2}) \leq 1$  meV and  $\Delta(^2P_{3/2} - ^2P_{1/2}) \sim 1.6$  meV. Consequently, the only major correction to be made is due to the spin-orbit splitting in  $\text{Si}(^3P)$ . The relevant

transition energies in Fig. 3 refer to energy differences between the lowest energy fine structure sublevels of the negative ion states and the lowest sublevel ( $^3P_0$ ) of the  $\text{Si}(^3P)$  state. The  $^3P_0$  level is computed to be 0.0186 eV below the  $\text{Si}(^3P)$  multiplet's "center of gravity"

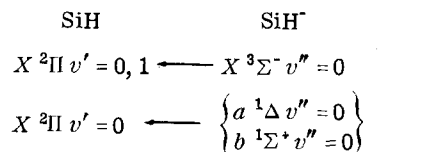
Table I compares the  $\text{Si}^-$  parameters determined in this experiment with previous values. Our value of the Si electron affinity, defined as the energy separation between  $\text{Si}^-(^4S)$  and  $\text{Si}(^3P_0)$ , is  $(1.385 \pm 0.005)$  eV. This number is in excellent agreement with the results of past theoretical, extrapolation, and experimental studies.<sup>6,7,10-14</sup> Of particular interest is the Hartree-Fock plus empirical correlation correction value of 1.39 eV of Clementi *et al.*<sup>6</sup> Similarly, our measured value for the  $\text{Si}^-(^2D)$  binding energy,  $(0.523 \pm 0.005)$  eV, is in agreement with both calculations and photodetachment work.<sup>6,7,10</sup> The  $\text{Si}^-(^2P)$  binding energy of  $(0.029 \pm 0.005)$  eV determined in this experiment is in reasonable agreement with the field ionization value,<sup>8,9</sup> 0.037 eV. The Hartree-Fock and model potential determinations of the  $^2P$  binding energy differ from ours by  $\sim 0.05$  eV and 0.04 eV, respectively.<sup>6,10</sup>

#### IV. $\text{SiH}^-$

##### A. Spectrum

Figure 2 shows the photoelectron spectra of  $^{28}\text{SiH}^-$  and  $^{29}\text{Si}^-$ . (The natural abundance of  $^{29}\text{Si}$  is 4.70%.) Of the seven observed peaks, four are assigned to  $^{28}\text{SiH}^-$  and two to  $^{29}\text{Si}^-$ . The seventh peak was shown to come from  $^{28}\text{SiH}_2^-$ , and was present as a result of the limited mass resolution of the Wien filter. The four peaks belonging to  $\text{SiH}^-$  are due to transitions between the three lowest electronic states of  $\text{SiH}^-(\sigma^2\pi^2\ ^3\Sigma^-, \ ^1\Delta, \ ^1\Sigma^+)$  and the ground electronic state of  $\text{SiH}(\sigma^2\pi \ X^2\Pi)$  in which a  $\pi$  electron is

detached.<sup>28</sup> The energy ordering of the  $\sigma^2\pi^2 \text{SiH}^-$  states is assumed to be the same as that of  $\text{NH}$  and  $\text{PH}(\ X^3\Sigma^- < a^1\Delta < b^1\Sigma^+)$ .<sup>15-18</sup> The four  $\text{SiH}^-$  peaks are specifically assigned to the following transitions:



The peaks are assigned to transitions arising from three separate negative ion states, because the relative peak intensities are altered when ion source conditions are changed. No evidence is seen for the transition  $a^4\Sigma^- \text{SiH} - X^3\Sigma^- \text{SiH}^-$ , presumably because this dipole-allowed process occurs at too high a detachment energy ( $> 2.25$  eV) for us to observe it. This limit is set by the difference between the photon energy (2.54 eV) and the minimum energy electrons which we can analyze ( $\sim 0.3$  eV). Wirsam's calculation<sup>29</sup> together with our measured  $\text{SiH}$  affinity predicts that electrons corresponding to the  $^4\Sigma^- - ^3\Sigma^-$  transition have 0.3 eV kinetic energy and therefore are unlikely to be detected by us. Transitions are observed from the  $^1\Delta$  and  $^1\Sigma^+$  states of  $\text{SiH}^-$  because these states, as the  $^2D$  and  $^2P$  states of  $\text{Si}^-$ , are sufficiently metastable to reach the interaction region. The  $a^1\Delta$  state is metastable because  $\Delta S \neq 0$  transitions (e.g., to  $X^3\Sigma^-$ ) are dipole forbidden.<sup>28</sup> The  $b^1\Sigma^+$  state is metastable with respect to  $X^3\Sigma^-$  for the same reason and is metastable with respect to  $a^1\Delta$  because  $\Delta\Lambda = 2$  transitions ( $\Lambda =$  electronic orbital angular momentum along the internuclear axis) are also dipole forbidden.<sup>30</sup> Transitions from these singlet states to  $^4\Sigma^- \text{SiH}$ , while energetically possible, are not expected to be observed, and in fact are not. The vertical detachment energies measured for the four  $\text{SiH} - \text{SiH}^-$  transitions are obtained in the following manner. The  $^2\Pi \text{SiH} - ^3\Sigma^- \text{SiH}^-$  transition is calibrated against the electron affinity of Si, determined in Sec. III. The  $^2\Pi \text{SiH} - ^1\Delta, \ ^1\Sigma^+ \text{SiH}^-$  transitions are then calibrated against the stronger  $^2\Pi - ^3\Sigma^-$  transition.

Since the detached electron comes from a nonbonding  $\pi$  orbital, it is expected that the equilibrium internuclear distances  $r_e$  of the  $X, a, b$  states of  $\text{SiH}^-$  and the  $X$  state of  $\text{SiH}$  will be very similar. (For  $X^1\Sigma \text{OH}^-$  and  $X^2\Pi \text{OH}$ , the equilibrium internuclear distances are virtually identical.)<sup>31</sup> Thus, we anticipate nearly diagonal Franck-Condon factors in the  $\text{SiH}^-$  photoelectron spectrum. Our resolution (50 meV) is insufficient to resolve vibrational sequences. Because the ion source vibrational temperature  $T_{\text{vib}} \leq 1000$  °K,<sup>31</sup> the sequences are labelled by the lowest possible quantum numbers (e.g.,  $v' = 0 - v'' = 0$  rather than  $v' = 1 - v'' = 1$ ) even though a small fraction of the intensity of the peaks must be ascribed to higher vibrational levels. (Double prime refers to the ion, single prime to the neutral.) For the very intense  $X^2\Pi(v' = 0)\text{SiH} - X^3\Sigma^-(v'' = 0)\text{SiH}^-$  transition, a  $v' = 1 - v'' = 0$  satellite is observed with intensity  $\sim \frac{1}{14}$  that of the diagonal transition (Fig. 2). Other nondiagonal vibrational transitions are not seen.

Our measured value for the vertical detachment energy of  $X^3\Sigma^- \text{SiH}^-$  is  $(1.276 \pm 0.006)$  eV, and our values for

TABLE I.  $\text{Si}^-$  binding energies (eV).

	Extrapolation	Theory	Previous experiment	This work <sup>a</sup>
$\text{Si}^-(3p^3^4S)$	1.36 $\pm$ 0.20 <sup>b</sup> 1.40 $\pm$ 0.10 <sup>c</sup> 1.36 <sup>d</sup> 1.46 <sup>h</sup>	1.39 <sup>e</sup> 1.41 <sup>f</sup>	$\sim 1.4$ <sup>d</sup>	$1.385 \pm 0.005$
$\text{Si}^-(3p^3^2D_{1/2})$		0.58 <sup>e</sup> 0.59 <sup>f</sup>	$0.56 \pm 0.04$ <sup>d</sup>	$0.523 \pm 0.005$
$\text{Si}^-(3p^3^2P_{1/2})$		0.08 <sup>e</sup> 0.065 <sup>f</sup>	$0.037 \pm ?$ <sup>g</sup>	$0.029 \pm 0.005$

<sup>a</sup>Relative to  $\text{Si}(^3P_0)$ . The binding energies reported here are slightly different from those reported in an earlier communication (A. Kasdan, E. Herbst, and W. C. Lineberger, in *Abstracts of IV International Conference on Atomic Physics*, edited by J. Kowalski and H. G. Weber (Univ. of Heidelberg, 1974), p. 246. The previous results had larger error bars, were based on a more approximate analysis, and are superseded by the above numbers.

<sup>b</sup>Reference 11.

<sup>c</sup>Reference 6 (Hartree-Fock).

<sup>d</sup>Reference 7 (photodetachment).

<sup>e</sup>Reference 14.

<sup>f</sup>Reference 10 (model potential).

<sup>g</sup>Reference 12.

<sup>h</sup>Reference 13.

<sup>i</sup>References 8, 9 (field ionization).

the vertical term energies of the excited SiH<sup>-</sup> states are

$$T(^1\Delta) = (0.568 \pm 0.005) \text{ eV},$$

$$T(^1\Sigma^+) = (1.049 \pm 0.005) \text{ eV}.$$

These vertical term energies  $T$  are simply the differences between the detachment energies of the two excited states and the detachment energy of the ground  $X^3\Sigma^-$  state.

The vertical detachment energies determined in our experiment are themselves differences between centers of gravity of large numbers of unresolved transitions, and corrections must be applied to obtain the usual spectroscopic parameters. Spectroscopic term energies and electron affinities most often refer to the lowest vibration-rotation levels of each electronic state, whereas our measured energies are admixtures of energies due to unresolved rotational and spin-orbit-split states. For example, the electron affinity (EA) of SiH is defined by the expression

$$\text{EA}(\text{SiH}) = E_{\text{eloc}} + G'(0) - G''(0) + F'_1(N=1), \quad (3)$$

where  $E_{\text{eloc}}$  is the energy difference between the potential minima of the ground states of SiH and SiH<sup>-</sup>,  $G'(0)$  and  $G''(0)$  are the zero-point energies of  $^2\Pi$  SiH and  $^3\Sigma^-$  SiH<sup>-</sup>, respectively, and  $F'_1(N=1)$  is the energy of the lowest rotational level of the lower spin-orbit component  $^2\Pi_{\text{SiH}}$ .<sup>28</sup> Measured vertical energies can be corrected approximately for these rotational and spin-orbit effects; these corrections, however, produce the dominant errors in our determined parameters. A detailed analysis of this subject is given in Sec. IV.C.

## B. Vibrational analysis

The  $v' = 0, 1$   $^2\Pi$  SiH -  $v'' = 0$   $^3\Sigma^-$  SiH<sup>-</sup> transitions have a measured separation of  $(1960 \pm 50) \text{ cm}^{-1}$ . Assuming rotational and spin-orbit contributions affect the two vertical energies similarly, the energy difference between the two peaks should correspond to the vibrational spacing  $G'(v'=1) - G'(v'=0)$  in  $^2\Pi$  SiH. Using the usual expansion for the energy levels of an anharmonic oscillator,<sup>28</sup> it is easily seen that

$$G'(1) - G'(0) = \omega_e - 2\omega_e x_e + \dots, \quad (4)$$

where  $\omega_e$  is the equilibrium harmonic frequency and  $\omega_e x_e$ , the first correction term. Spectroscopically obtained values for  $\omega_e - 2\omega_e x_e$  of  $^2\Pi$  SiH,  $(1973 \pm 13) \text{ cm}^{-1}$ ,<sup>32</sup> and  $1971.1 \text{ cm}^{-1}$ ,<sup>33</sup> are in excellent agreement with our work.

From the intensity ratio of the  $v' = 1 - v'' = 0$  to the  $v' = 0 - v'' = 0$  transition, we can, via a harmonic oscillator Franck-Condon analysis, determine the magnitude of the difference in equilibrium internuclear distance between  $^2\Pi$  SiH and  $^3\Sigma^-$  SiH<sup>-</sup>. Because the internuclear distance  $r_e$  of  $X^3\Sigma^-$  PH (isoelectronic with SiH<sup>-</sup>) is  $0.09 \text{ \AA}$  smaller than that of  $^2\Pi$  SiH, we believe a strong reason exists for postulating that  $r_e''(^3\Sigma^- \text{SiH}^-) < r_e'(^2\Pi \text{SiH})$ .<sup>28</sup> The vibrational frequency  $\omega_e''$  of  $^3\Sigma^-$  SiH<sup>-</sup> is not determined by our experiment, since no distinct "hot" bands are observed. However, it is easily ascertained that the Franck-Condon analysis is quite insensitive to the assumed value of  $\omega_e''$ . Initially, we assume for convenience

that  $\omega_e''(\text{SiH}^-) \cong \omega_e'(\text{SiH}) = 2045 \text{ cm}^{-1}$ .<sup>32</sup> Then, using the value  $r_e' = (1.520 \pm 0.001) \text{ \AA}$  for SiH,<sup>32</sup> and the assumption that  $r_e'' < r_e'$ , we obtain  $r_e'' = 1.473 \text{ \AA}$ . Utilizing Badgers' Rule<sup>34</sup> (with constants modified to obtain  $\omega_e$  to within 1% of the true value for the ground state of SiH), it is found that  $\omega_e''(^3\Sigma^- \text{SiH}^-) = 2175 \text{ cm}^{-1}$ . If this value of  $\omega_e''$  is used in our Franck-Condon analysis, we obtain a new value of  $r_e'' = 1.474 \text{ \AA}$ . Our "iterative" Franck-Condon approach converges to these "final" values of  $r_e''$ ,  $\omega_e''$ . (If, instead of  $\omega_e'$  and  $\omega_e''$ ,  $\omega_e' - 2\omega_e' x_e''$  and  $\omega_e'' - 2\omega_e'' x_e''$  are used in the calculation, the final  $r_e''$  determined differs by  $0.001 \text{ \AA}$ .) The total error in the determination of  $r_e''$  is at most  $0.004 \text{ \AA}$  (assuming  $r_e'' < r_e'$ ). This error stems from four sources: error in the measurement of the intensity ratio ( $0.001 \text{ \AA}$ ), error in the spectroscopically-determined value of  $r_e'$  ( $0.001 \text{ \AA}$ ), error due to uncertainty in  $\omega_e''$  ( $0.001 \text{ \AA}$ ), and error due to the harmonic overlap approximation ( $0.001 \text{ \AA}$ ).

Only diagonal vibrational transitions are seen between the  $a^1\Delta$  and  $b^1\Sigma^+$  states of SiH<sup>-</sup> and the  $^2\Pi$  state of SiH. Assuming that  $r_e'' < r_e(^1\Delta, ^1\Sigma^+) < r_e'$ , we conclude from this that  $r_e$  in both the  $^1\Delta$  and  $^1\Sigma^+$  states is  $\sim 1.50 \pm 0.05 \text{ \AA}$ . An empirical rule<sup>28</sup> then tells us that  $\omega_e \sim 2100 \text{ cm}^{-1}$  in these states. (All spectroscopic information determined for SiH<sup>-</sup> is tabulated in Table II.)

## C. Errors in measured vertical energies

In order to obtain values for the electron affinity of SiH and the term energies ( $T_0$ ) of the SiH<sup>-</sup> excited states, we must correct for rotational and spin-orbit effects included in our measured detachment energies. The  $X^2\Pi$  state of SiH is intermediate between Hund's cases (a) and (b),<sup>28</sup> with  $A_0$ , the spin-orbit coupling constant for  $v = 0$ ,  $143.35 \text{ cm}^{-1}$ , and  $B_0$ , the rotational constant for  $v = 0$ ,  $7.391 \text{ cm}^{-1}$ .<sup>33</sup> Spin-orbit splittings for rotational energy levels reached via transitions from SiH<sup>-</sup> are  $\geq 50 \text{ cm}^{-1}$ ,<sup>35</sup> and must be considered in this treatment. Spin-spin and spin-rotation effects in  $^3\Sigma^-$  SiH<sup>-</sup> can be neglected. Diatomic rotational levels in this state can then be represented by the well known formula<sup>28</sup>

$$F'' = B_0'' N(N+1); \quad N \geq 0, \quad (5)$$

where  $B_0''$  is the rotational constant for vibrational state  $v'' = 0$  and  $N$  is the end-over-end angular momentum. For the  $v' = 0$   $^2\Pi$  SiH state, the spin-orbit-split rotational series  $F'_1$  and  $F'_2$  are, using a case (b) basis set, given by the expressions<sup>28</sup>

$$F'_2(N) = B_0' \left\{ N^2 - 1 + \frac{1}{2} \left[ 4N^2 + \frac{A_0}{B_0} \left( \frac{A_0}{B_0} - 4 \right) \right]^{1/2} \right\},$$

$$F'_1(N) = B_0' \left\{ (N+1)^2 - 1 - \frac{1}{2} \left[ 4(N+1)^2 + \frac{A_0}{B_0} \left( \frac{A_0}{B_0} - 4 \right) \right]^{1/2} \right\}; \quad (6)$$

$$N \geq 1,$$

where, for SiH,  $F'_2(N) > F'_1(N)$  for all  $N$ .

The negative ion rotational distribution  $p(N)$  in the  $^3\Sigma^-$  state is assumed to be represented by a rotational temperature  $T_r$ . It is then assumed that the centroid  $E$  of the measured detachment peak for the process  $X^2\Pi(v' = 0)\text{SiH} - X^3\Sigma^-(v'' = 0)\text{SiH}^-$  corresponds to the ensemble

TABLE II. Constants determined for SiH<sup>-</sup>.

	$X^3\Sigma^-$	$a^1\Delta$	$b^1\Sigma^+$
EA (eV) <sup>a</sup>	1.277 ± 0.009		
$T_0$ (eV)		0.568 ± 0.012	1.049 ± 0.012
$\omega_e$ (cm <sup>-1</sup> ) <sup>b</sup>	2175.00 ± 50	~2100	~2100
$r_e$ (Å)	1.474 ± 0.004	1.50 ± 0.05	1.50 ± 0.05
$D_0$ (eV) <sup>c</sup>	2.99 ± 0.02	3.29 ± 0.02	3.30 ± 0.02

<sup>a</sup>Cade<sup>37</sup> has predicted a value of (1.46 ± 0.30) eV.

<sup>b</sup>These values are obtained by empirical rules.

<sup>c</sup>These values are based on a dissociation energy of 25 000 cm<sup>-1</sup> for <sup>2</sup>Π SiH—see text.

average of the energies of  $\Delta N=0$  transitions from rotational levels of <sup>3</sup>Σ<sup>-</sup> SiH<sup>-</sup> to the centers of gravity of spin-orbit-split rotational levels of <sup>2</sup>Π SiH. In mathematical terms, we assume that

$$E = EA(\text{SiH}) + \sum_{N=1}^{\infty} p(N) \frac{[g_1 F'_1(N) + g_2 F'_2(N)]}{g_1 + g_2} - \left[ \sum_{N=1}^{\infty} p(N) B'_0 N(N+1) \right] - F'_1(N=1), \quad (7)$$

where  $g_2 = 2N$  and  $g_1 = 2N + 2$  are the statistical weights of  $F'_2$  and  $F'_1$ . The electron affinity of SiH, defined by Expression (3), corresponds to the transition from  $v'' = 0$ ,  $N'' = 0$  <sup>3</sup>Σ<sup>-</sup> SiH<sup>-</sup> to  $v' = 0$ ,  $F'_1(N=1)$  of <sup>2</sup>Π SiH. The measured detachment energy adds to this value the average rotational energy of the neutral after being formed in  $\Delta N=0$  transitions [expressed relative to  $F'_1(N=1)$ ] and subtracts the average rotational energy of the ion. The error in Expression (7) is estimated to be of the order of magnitude of a rotational constant for a pure case (b) ( $A=0$ ) neutral state where neglected  $\Delta N = \pm 1$  effects provide the major source of error. For <sup>2</sup>Π SiH, intermediate between Hund's cases (a) and (b), the center of gravity assumption provides an additional source of error. However, the major error in this analysis is not the theoretical form of Expression (7) but the assumption of a well known, well defined ion source rotational temperature. If we assume that  $T_r \sim 1000$  °K,<sup>31</sup> and that  $r_e'' < r_e'$ , (see Sec. IV.B), we have enough knowledge to utilize Eq. (7) (assuming that  $B'_0/B'_1 = B''_0/B''_1$ ) and to obtain by numerical analysis

$$EA(\text{SiH}) = E + 5.0 \text{ cm}^{-1} \quad (1 \text{ cm}^{-1} = 0.124 \text{ meV}).$$

The small difference between EA and  $E$  is due to a fortuitous cancellation of rotational and spin-orbit terms. A more realistic appraisal of our knowledge of  $T_r$ , however, suggests that  $500$  °K  $\leq T_r \leq 1500$  °K.<sup>31</sup> This uncertainty in  $T_r$  adds a maximum of  $\pm 25$  cm<sup>-1</sup> uncertainty to our calculated difference between EA and  $E$ . To be safer, we assume the uncertainty in our theoretical correction to be  $\pm 50$  cm<sup>-1</sup> ( $\pm 0.006$  eV). The total error in the affinity determination is then the vector sum of this error and the experimental measurement error; viz.,

$$EA(\text{SiH}) = (1.277 \pm 0.009) \text{ eV},$$

where the reported affinity includes our correction.

For detachment transitions arising from excited electronic states of SiH<sup>-</sup>, this type of error analysis is more

difficult to perform because the rotational constants of these states are not well determined by our experiment and because the rotational temperatures of such excited states are very poorly understood. We believe that vertical transitions arising from the <sup>1</sup>Δ and <sup>1</sup>Σ<sup>+</sup> states of SiH<sup>-</sup> are within  $\pm 0.010$  eV of the corresponding affinities. Total errors for the term values ( $T_0$ ) of these states, reported in Table II, are  $\pm 0.012$  eV.

#### D. Dissociation energies and discussion

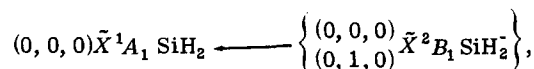
Once the proper dissociation limits are chosen, it is possible to calculate the dissociation energies  $D_0$  of the  $X$ ,  $a$ , and  $b$  states of SiH<sup>-</sup> given knowledge of the dissociation energy of  $X^2\Pi$  SiH. The  $X^3\Sigma^-$  state of SiH<sup>-</sup> clearly correlates with the ground states of Si<sup>-</sup> and H—Si<sup>-</sup>(<sup>4</sup>S<sub>u</sub>) and H(<sup>2</sup>S<sub>g</sub>). The lowest energy dissociation products that can correlate with <sup>1</sup>Δ SiH<sup>-</sup> are Si<sup>-</sup>(<sup>2</sup>D<sub>u</sub>) and H(<sup>2</sup>S<sub>g</sub>). Likewise, <sup>1</sup>Σ<sup>+</sup> SiH<sup>-</sup> must, for reasons of symmetry, correlate with Si<sup>-</sup>(<sup>2</sup>P<sub>u</sub>) + H(<sup>2</sup>S<sub>g</sub>).<sup>28</sup> Thus, each of the three observed states of Si<sup>-</sup> correlates with an observed state of SiH<sup>-</sup>. With knowledge of the term energies of the various Si<sup>-</sup> and SiH<sup>-</sup> states and the electron affinities of Si and SiH, determination of the dissociation energies  $D_0$  is now a simple algebraic procedure. Unfortunately,  $D_0(X^2\Pi \text{ SiH})$  is poorly known<sup>32,33,36</sup> but is probably  $\sim 25$  000 cm<sup>-1</sup>. If we use this value, we derive the dissociation energies listed in Table I.

It is interesting to compare the singlet-triplet ( $a^1\Delta - X^3\Sigma^-$ ) intercombination separations in SiH<sup>-</sup> and its iso-electronic species PH and SH<sup>+</sup>. Cade<sup>18</sup> has calculated this splitting for the latter two species, obtaining 0.95 eV and 1.16 eV for PH and SH<sup>+</sup>, respectively. Our measured value for SiH<sup>-</sup>, (0.568 ± 0.012) eV, is clearly much smaller than either of Cade's values. It should be noted that the intercombination differences (<sup>4</sup>S—<sup>2</sup>D) in the corresponding atoms—Si<sup>-</sup>, P, and S<sup>+</sup>—follow the same trend (0.862 eV < 1.409 eV < 1.841 eV).<sup>25</sup>

In another paper, Cade<sup>37</sup> has calculated the electron affinity of SiH to be (1.46 ± 0.30) eV, which is in accord with our measured value of (1.277 ± 0.009) eV.

#### V. SiH<sub>2</sub><sup>-</sup>

The photoelectron spectrum of <sup>28</sup>SiH<sub>2</sub><sup>-</sup> is depicted in Fig. 4. Several of the observed peaks belong to different species of the same mass—<sup>29</sup>SiH<sub>2</sub><sup>-</sup> or <sup>30</sup>Si<sup>-</sup>. (The natural abundances of <sup>29</sup>Si and <sup>30</sup>Si are 4.7% and 3.09%, respectively.) Only three features in the spectrum can be clearly identified as belonging to <sup>28</sup>SiH<sub>2</sub><sup>-</sup>—the dominant peak at electron energy 1.41 eV, a satellite hot band at 1.56 eV, and a diffuse unresolved feature that sets in at  $\sim 0.8$  eV. The diffuse cutoff of this feature near  $\sim 0.3$  eV is due to the transmission cutoff of the electron energy analyzer and has no physical significance for SiH<sub>2</sub><sup>-</sup>. The dominant feature and its satellite are easily assigned to the transitions



respectively. The numbers in parentheses refer to the customary vibrational quantum numbers  $v_1, v_2, v_3$ .<sup>38</sup> The ground state of SiH<sub>2</sub><sup>-</sup> is assumed to have the same

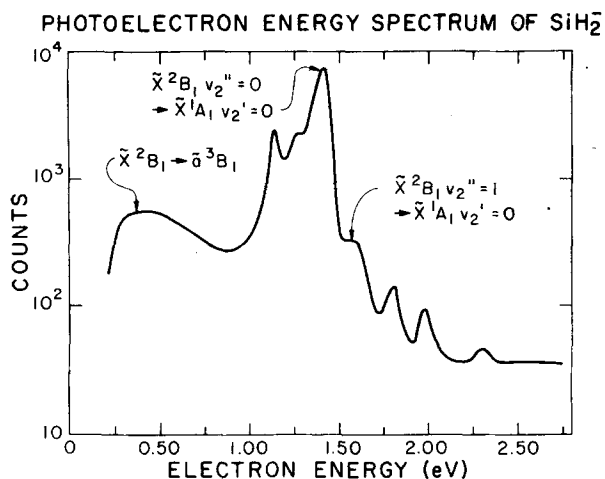


FIG. 4. The photoelectron spectrum of  $\text{SiH}_2^-$ . The cutoff of the diffuse feature at an electron energy of  $\sim 0.3$  eV is due to the transmission cutoff of the analyzer. All unlabeled peaks are due to  $^{30}\text{Si}^-$  and  $^{29}\text{SiH}^-$ .

$^2B_1$  symmetry (point group  $C_{2v}$ ) as that of  $\text{PH}_2$ <sup>39</sup> (isoelectronic species) and a molecular orbital configuration  $(1a_1)^2(1b_2)^2(2a_1)^2(1b_1)^1$ . In the above photoelectron transition, the  $(1b_1)$  electron is detached. If, instead, one  $(2a_1)$  electron were detached, the  $\text{SiH}_2$  produced would be in its  $^3B_1$  state—which is the ground state in the analogous  $\text{CH}_2$  molecule.<sup>20</sup> In  $\text{SiH}_2$ , the  $^3B_1$  state has not been previously observed, but calculations place its zero-point energy at 0.2 eV relative to the ground  $^1A_1$  state.<sup>21</sup> It is our contention that the diffuse feature in the  $\text{SiH}_2^-$  spectrum can be assigned to the transition  $^3B_1 \text{SiH}_2^- \rightarrow ^2B_1 \text{SiH}_2^-$ ; this will be discussed later.

The spectrum corresponding to the  $^1A_1 \rightarrow ^2B_1$  transition shows that the Franck-Condon factors are nearly diagonal, as expected. The geometric parameters<sup>40</sup> of  $^1A_1 \text{SiH}_2$  are  $r_0 = 1.516 \text{ \AA}$ ,  $\theta_0 = 92^\circ 5'$ ; those of  $^2B_1 \text{SiH}_2^-$  are unknown. In the isoelectronic molecule  $^2B_1 \text{PH}_2$ ,  $r_0 = 1.43 \text{ \AA}$ ,  $\theta_0 = 91^\circ 40'$ .<sup>39</sup> Because the internuclear distances in the ground states of  $\text{SiH}_2$  and  $\text{PH}_2$  are very similar to those of  $\text{SiH}$  and  $\text{PH}$ , we presume that  $^2B_1 \text{SiH}_2^-$  behaves in a similar manner and that (see Table II)  $r_e \sim 1.47 \text{ \AA}$ . It is expected that the bond angle of  $^2B_1 \text{SiH}_2^-$  is much the same as those of  $^2B_1 \text{PH}_2$  and  $^1A_1 \text{SiH}_2$ ; viz.,  $\theta \sim 91^\circ - 92^\circ$ . Thus, we anticipate that  $^2B_1 \text{SiH}_2^-$  and  $^1A_1 \text{SiH}_2$  have similar geometries and that the detachment transition between them has only weak nondiagonal Franck-Condon components. As in the  $^2\Pi \text{SiH}^- \rightarrow ^3\Sigma^- \text{SiH}^-$  transition, the electron ejected (in this case of  $1b_1$  symmetry) is presumably nonbonding.

The vertical detachment energy measured for the dominant  $[(0, 0, 0) \rightarrow (0, 0, 0)]$  peak of the  $\tilde{X}^1A_1 \text{SiH}_2^- \rightarrow \tilde{X}^2B_1 \text{SiH}_2^-$  spectrum is  $(1.124 \pm 0.003) \text{ eV}$ . The electron affinity of  $\text{SiH}_2$  is defined as the energy difference between the zero-point vibrational levels of  $\tilde{X}^1A_1 \text{SiH}_2^-$  and  $\tilde{X}^2B_1 \text{SiH}_2^-$ . To obtain rigorously the  $\text{SiH}_2$  electron affinity from our measured vertical detachment energy, the blending of various asymmetric top rotational transitions in our data would have to be considered. Given the apparent similarity in geometry and, hence, rotational constants in the two states, we believe that rotational

effects cannot shift our vertical detachment energy from the true  $\text{SiH}_2$  affinity by more than 0.01–0.02 eV. We thus obtain a value of

$$EA(\text{SiH}_2) = (1.124 \pm 0.020) \text{ eV}$$

for the affinity. Our value is in favorable agreement with the recent photodetachment studies by Smyth,<sup>41</sup> who places the photodetachment threshold for  $\text{SiH}_2^-$  at  $\approx 1.11 \text{ eV}$ .

One hot band is seen in the  $^1A_1 \rightarrow ^2B_1$  spectrum; this is assigned to the  $(0, 0, 0) \rightarrow (0, 1, 0)$  transition. From the difference in vertical energy between the main peak and the hot band, we are able to obtain a rough value for the  $\text{SiH}_2^-$  bending frequency:

$$\omega_2''(\text{SiH}_2^-) = (1200 \pm 160) \text{ cm}^{-1}.$$

This value is comparable to  $\omega_2(^2B_1 \text{PH}_2) = 1101 \text{ cm}^{-1}$ .<sup>30</sup>

The  $^3B_1$  state of  $\text{SiH}_2$  has been calculated to have a geometry of  $r_e = 1.55 \text{ \AA}$ ,  $\theta_e = 123.5^\circ$ .<sup>21</sup> Since the bond angle in  $^2B_1 \text{SiH}_2^-$  is almost certainly  $< 100^\circ$ , the transition  $^3B_1 \text{SiH}_2 \rightarrow ^2B_1 \text{SiH}_2^-$  involves a large change in bond angle. As is customary in such cases,<sup>38</sup> a long progression in the bending vibrational mode of the upper state is expected. Wirsam<sup>21</sup> calculates the bending frequency of  $^3B_1 \text{SiH}_2$  to be  $764 \text{ cm}^{-1}$ . The bending frequency of  $^2B_1 \text{SiH}_2^-$  has been determined by us to be  $1200 \text{ cm}^{-1}$ . If we assume that the ion source vibrational temperature is such that  $v_2'' = 0, 1$  are the only levels of sufficient population to be of importance, and if we also assume (see below, however) that the  $^3B_1$  bending mode is nearly harmonic, then we would predict the observation of two progressions (one separated from the other by  $1200 \text{ cm}^{-1}$ ) in  $v_2'$ , both with peaks every  $764 \text{ cm}^{-1}$ :



The two progressions would overlap one another to such an extent that peaks would not be resolvable by our electron monochromator. This analysis is somewhat simplistic since  $^3B_1 \text{SiH}_2$  is a quasilinear molecule with a potential maximum of at most 0.5 eV in its linear configuration.<sup>21</sup> In any case, the diffuse feature in the  $\text{SiH}_2^-$  spectrum is assigned to the transition from the ground state of  $\text{SiH}_2^-$  to the lowest triplet state of  $\text{SiH}_2$ . From the onset of the diffuse feature, an approximate upper bound to the zero-point triplet energy in  $\text{SiH}_2$  can be obtained:  $T_0(^3B_1) \leq 0.6 \text{ eV}$ . We are only able to obtain an upper bound because we do not know at which  $v_2'$  level the diffuse features onsets. This upper limit is in agreement with Wirsam's calculated value of 0.2 eV.<sup>21</sup>

## VI. SUMMARY

We have applied laser photoelectron spectrometry techniques to the study of  $\text{Si}^-$ ,  $\text{SiH}^-$ , and  $\text{SiH}_2^-$  in order to obtain the electron affinities of the neutral species and to determine whether these negative ions possess bound excited states. We have observed three electronic states in both  $\text{Si}^-$  and  $\text{SiH}^-$  and have analyzed their spectroscopic constants. From the ground state of  $\text{SiH}_2^-$ , we have observed transitions to both the  $X^1A_1$  and  $\tilde{a}^3B_1$  states of  $\text{SiH}_2$  and have determined an upper limit for the energy spacing between them.

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