

# Photoionization mass spectrometric studies of the transient species $\text{Si}_2\text{H}_n$ ( $n=2-5$ )

B. Ruscic and J. Berkowitz

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 13 February 1991; accepted 9 May 1991)

The transient species  $\text{Si}_2\text{H}_5$ ,  $\text{Si}_2\text{H}_4$ ,  $\text{Si}_2\text{H}_3$ , and  $\text{Si}_2\text{H}_2$  have been prepared for the first time, by reactions of F atoms with  $\text{Si}_2\text{H}_6$ . The species are generated *in situ* and studied by photoionization mass spectrometry. The adiabatic ionization potentials are (in eV)  $\text{Si}_2\text{H}_5$ ,  $7.60 \pm 0.05$ ;  $\text{Si}_2\text{H}_4$ ,  $8.09 \pm 0.03$ ;  $\text{Si}_2\text{H}_3$ ,  $< 7.59$ ; and  $\text{Si}_2\text{H}_2$ ,  $8.20 \pm_{0.02}^{0.01}$ . In addition, two fragment appearance potential curves were measured,  $\text{Si}_2\text{H}_3^+$  ( $\text{Si}_2\text{H}_5$ ) and  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_4$ ). By combining these ionization potentials with appearance potentials obtained here and from  $\text{Si}_2\text{H}_6$ , the following heats of formation (kcal/mol at 0 K) have been inferred:  $\text{Si}_2\text{H}_5$ ,  $< 63.3$  (59.2);  $\text{Si}_2\text{H}_4$ ,  $67.9 \pm 0.9$ ;  $\text{Si}_2\text{H}_3$  ( $\sim 96$ );  $\text{Si}_2\text{H}_2$ ,  $< 100.7$  (90.2–95.6). The quantities in parentheses are probable values, but less well defined. Structures and structural changes resulting from photoionization are discussed. In particular,  $\text{Si}_2\text{H}_2$  and its cation are very likely cyclic (doubly bridged). Heats of formation of cations are also obtained, from which the proton affinities of  $\text{Si}_2\text{H}_2$  ( $199 \pm 3$  kcal/mol) and  $\text{Si}_2\text{H}_4$  (199.9 kcal/mol) are deduced. The structural and energetic differences between corresponding silicon and carbon hydrides are discussed in detail.

## I. INTRODUCTION

The heats of formation of the species  $\text{C}_2\text{H}_n$  ( $n=1-6$ ) are now known to acceptable chemical accuracy ( $< \pm 2$  kcal/mol). Alternatively, one can state that the C–H bond energies corresponding to successive H-atom loss are also known to this accuracy. Experimentally, such studies are made less difficult by the fortunate circumstance that not only  $\text{C}_2\text{H}_6$ , but also  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  are stable species whose heats of formation can be measured accurately by classical techniques (e.g., combustion calorimetry). Consequently, the major tasks in establishing the successive H-atom loss energies consist of establishing  $\Delta H_f(\text{C}_2\text{H}_5)$ ,  $\Delta H_f(\text{C}_2\text{H}_3)$ , and  $\Delta H_f(\text{C}_2\text{H})$ . These three quantities have been determined to acceptable chemical accuracy by several methods in recent years.<sup>1</sup>

By contrast, corresponding experimental studies on the  $\text{Si}_2\text{H}_n$  species are much less advanced. In this system, only  $\text{Si}_2\text{H}_6$  appears to be stable enough to study by classical means, and in fact its heat of formation has been measured.<sup>2</sup> However,  $\text{Si}_2\text{H}_4$  and  $\text{Si}_2\text{H}_2$  have not been isolated for study, nor have  $\text{Si}_2\text{H}_5$ ,  $\text{Si}_2\text{H}_3$ , and  $\text{Si}_2\text{H}$ . The reasons for this difference in behavior of carbon and silicon hydrides are very likely connected with the greater difficulty of silicon in forming double and triple bonds, compared to carbon. Since all of the  $\text{Si}_2\text{H}_n$  ( $n=1-5$ ) are transient species, classical means for determining their heats of formation are not tractable. The information regarding these species which exists to date is largely based on *ab initio* calculations,<sup>3-15</sup> although some experimental information exists from modeling of kinetic data.<sup>16-19</sup>

One way of determining the heat of formation of a transient species is to determine the heat of formation of the cation, and independently the ionization potential of the desired species. An accurate determination of the heat of formation of a cation is rather straightforward with photoionization mass spectrometry, if the cation appears as a "favorable" fragment from some larger molecular entity.

The term "favorable" implies that the fragment is the one of lowest (or possibly second lowest) decomposition energy, and that it can occur without significant reverse activation energy. Thus,  $\Delta H_f(\text{C}_2\text{H}_3^+)$  can be determined accurately by measuring the appearance potential of  $\text{C}_2\text{H}_3^+$  from  $\text{C}_2\text{H}_4$ , but not from  $\text{C}_2\text{H}_6$ , since in this latter case it is preceded by the  $\text{C}_2\text{H}_5^+$  and  $\text{C}_2\text{H}_4^+$  fragments and is consequently subject to a kinetic shift, or delayed onset.<sup>20</sup> However, the heat of formation of  $\text{C}_2\text{H}_3^+$  derived from  $\text{C}_2\text{H}_4$ , together with the measured ionization potential of  $\text{C}_2\text{H}_3$ , yields a fairly accurate value for  $\Delta H_f(\text{C}_2\text{H}_3)$ .<sup>21</sup>

The relevance of this observation to the study of disilane decomposition must be kept in mind. The appearance potentials<sup>22</sup> of  $\text{Si}_2\text{H}_5^+$  and  $\text{Si}_2\text{H}_4^+$  from  $\text{Si}_2\text{H}_6$  (see preceding paper) are likely to be thermochemically significant, but the appearance energies of  $\text{Si}_2\text{H}_n^+$  ( $n=1-3$ ) all can be expected to display a delayed onset. In order to obtain accurate heats of formation of  $\text{Si}_2\text{H}_3^+$  and  $\text{Si}_2\text{H}_2^+$ , it is best to start with  $\text{Si}_2\text{H}_5$  and  $\text{Si}_2\text{H}_4$ , since  $\text{H}_2$  loss corresponds to the first fragmentation of the corresponding cation. However, neither  $\text{Si}_2\text{H}_5$  nor  $\text{Si}_2\text{H}_4$  are stable. Each must be prepared in a steady-state system, and upon photoionization, a fragmentation threshold must be determined. This presents a higher order of difficulty than, for example, determining the appearance potential  $\text{C}_2\text{H}_3^+$  ( $\text{C}_2\text{H}_4$ ). In addition, one must contend with the problem of accumulated errors. Thus,  $\Delta H_f^0(\text{Si}_2\text{H}_4)$  can be determined by the method outlined above, but with an error typically larger than that which can be obtained for  $\text{C}_2\text{H}_4$  from bomb calorimetry. However, this newly found  $\Delta H_f^0(\text{Si}_2\text{H}_4)$  serves as the starting point for determining  $\Delta H_f^0(\text{Si}_2\text{H}_2)$ . With these caveats, we have undertaken the study of the transient species produced *in situ* when F atoms react with  $\text{Si}_2\text{H}_6$ .

## II. EXPERIMENTAL ARRANGEMENT

The transient species  $\text{Si}_2\text{H}_n$  ( $n=2-5$ ) were prepared *in situ* by the reaction of F atoms with  $\text{Si}_2\text{H}_6$ . The fluorine

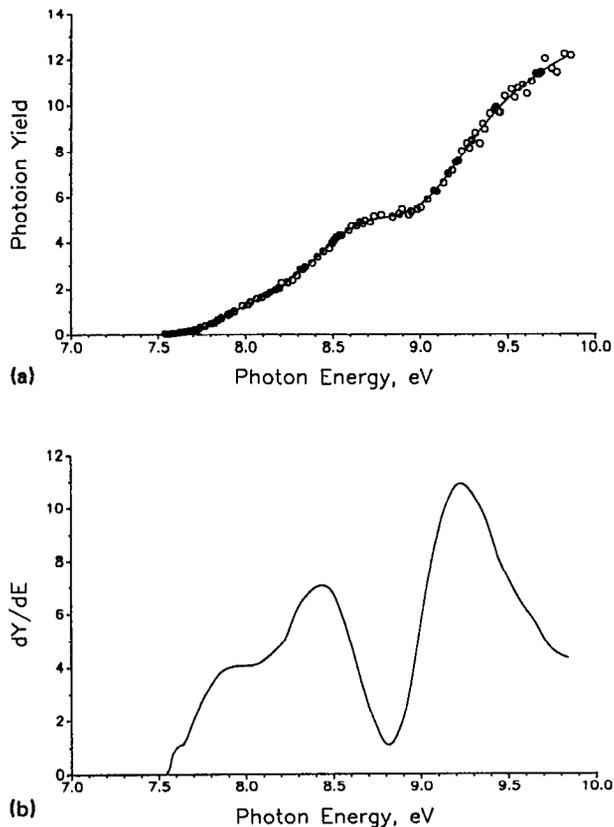


FIG. 1. (a) The photoion yield curve of  $\text{Si}_2\text{H}_5^+$  ( $\text{Si}_2\text{H}_5$ ). The continuous curve is a spline function fitted to the data. (b) The derivative of the fitted curve in (a), simulating the photoelectron spectrum.

atoms were generated in a microwave discharge through pure  $\text{F}_2$ . The description of the flow tube and reaction cup has been given previously, as has the photoionization mass spectrometric method.<sup>23</sup> Disilane was obtained from Matheson Gas Products. Most of the measurements were performed utilizing the peak light intensities in the many-line emission spectrum of a discharge in molecular hydrogen. The nominal wavelength resolution was  $0.84 \text{ \AA}$  (full width at half-maximum).

### III. EXPERIMENTAL RESULTS

#### A. $\text{Si}_2\text{H}_5$

##### 1. The parent ion

In the reaction of F atoms with  $\text{Si}_2\text{H}_6$ , the free radical  $\text{Si}_2\text{H}_5$  is produced by hydrogen abstraction. The photoion yield curve obtained,  $\text{Si}_2\text{H}_5^+$  ( $\text{Si}_2\text{H}_5$ ), is presented in Fig. 1(a). One observes a gradual, almost linear approach to threshold in the region  $\sim 8.6-7.6 \text{ eV}$ . This is indicative of a significant change in geometry between  $\text{Si}_2\text{H}_5$  and  $\text{Si}_2\text{H}_5^+$ . At higher photon energy, the ion yield has a short plateau, followed by another enhancement in intensity. A spline function fitted to this experimental curve is also shown in Fig. 1(a).

If photoionization in this instance can be described as direct ionization, characterized by step-function behavior, then the derivative of this function should simulate a photoelectron spectrum. The derivative of the spline function of

Fig. 1(a) is given in Fig. 1(b). Two features are apparent—a partially resolved band with maxima at  $\sim 7.9$  and  $8.4 \text{ eV}$ , and a more isolated higher-energy band with a maximum at  $9.25 \text{ eV}$ . These maxima should correspond to vertical ionization potentials for formation of different states (or structures) of  $\text{Si}_2\text{H}_5^+$ . In addition, there is a weak band near threshold, which could be a "hot band." The general features of this derivative function are not strongly dependent upon the degree of smoothing utilized to fit the experimental curve of Fig. 1(a). The adiabatic ionization potential is chosen to be  $7.60 \pm 0.05 \text{ eV}$ . The relatively large error bar is partially due to poorer statistics near threshold, and partially to allow for the possible presence of some vibrationally excited  $\text{Si}_2\text{H}_5$ . In our earlier study of  $\text{SiH}_3$  formed by the  $\text{F} + \text{SiH}_4$  reaction, a very weak onset was observed<sup>23(b)</sup> which was shown to be due to photoionization from a  $v'' = 1$  thermally populated state of  $\text{SiH}_3$ .<sup>24</sup> The deviation between vertical I.P. ( $7.9 \text{ eV}$ ) and adiabatic I.P. ( $7.60 \pm 0.05 \text{ eV}$ ) is a measure of the change of molecular structure between the ground states of  $\text{Si}_2\text{H}_5$  and  $\text{Si}_2\text{H}_5^+$ .

##### 2. The $\text{Si}_2\text{H}_3^+$ fragment

Under the experimental conditions ( $\text{F} + \text{Si}_2\text{H}_6$  reaction) favorable for formation of  $\text{Si}_2\text{H}_5$ , a signal corresponding to  $\text{Si}_2\text{H}_3^+$  could be observed at lower energies than its threshold from  $\text{Si}_2\text{H}_6$ . The photoion yield curve of  $\text{Si}_2\text{H}_3^+$  obtained under these conditions, attributed to  $\text{H}_2$  loss from  $\text{Si}_2\text{H}_5^+$  and designated  $\text{Si}_2\text{H}_3^+$  ( $\text{Si}_2\text{H}_5$ ), is shown in Fig. 2(a). A spline function fitted to the experimental data dis-

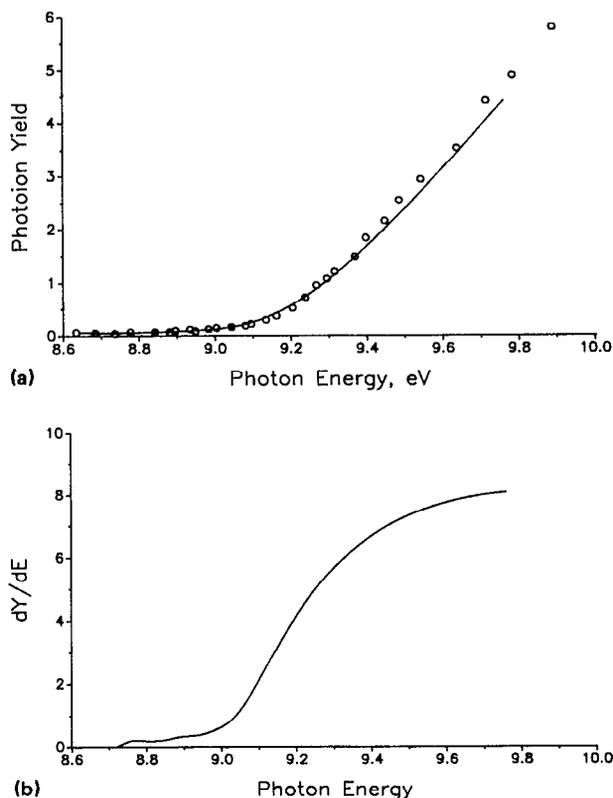


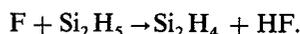
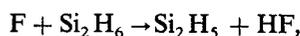
FIG. 2. (a) The photoion yield curve of  $\text{Si}_2\text{H}_3^+$  ( $\text{Si}_2\text{H}_5$ ). A spline function fitted to the experimental points is also shown. (b) The derivative of the fitted curve in (a), simulating a portion of the breakdown diagram.

plays significant curvature. At a magnification of a factor 4, one sees either a tailing toward the background level or a weak onset, followed by a large and linear increase in intensity. The extrapolation of the latter to a sloping background (or sloping weak threshold) yields  $9.15 \pm 0.02$  eV. Figure 2(b) displays the derivative of this function. The reason for obtaining a derivative curve in this case is not the same as in Fig. 1, where we have tried to simulate a photoelectron spectrum. Here, the purpose is to simulate a breakdown diagram, or photoion-photoelectron coincidence experiment. The derivative has a long tail which extends to  $\sim 8.74$  eV, as well as the strong process. The latter appears shifted to lower energy, probably because of the coarseness of the spline fit. A tighter fit results in oscillations in the tail region.

## B. $\text{Si}_2\text{H}_4$

### 1. The parent ion

In the  $\text{F} + \text{Si}_2\text{H}_6$  experiment, photoionization producing  $\text{Si}_2\text{H}_4^+$  is observed at much lower photon energy than from  $\text{Si}_2\text{H}_6$  alone. It can also be inferred from the onset energy, and from the relative intensities of  $\text{Si}_2\text{H}_4^+$  and  $\text{Si}_2\text{H}_5^+$  with variation of  $\text{F}$  and/or  $\text{Si}_2\text{H}_6$  flow rates, that the  $\text{Si}_2\text{H}_4^+$  observed at these lower energies results from ionization of neutral  $\text{Si}_2\text{H}_4$ . The latter is presumed to be formed in the reaction cell by sequential H-atom abstraction, i.e.,



Several studies<sup>3,9</sup> have noted that pyrolysis of  $\text{Si}_2\text{H}_6$  (loss of  $\text{H}_2$ ) could result in two structures—the more-stable  $\text{H}_2\text{Si-SiH}_2$ , whose direct formation requires the surmounting of a large activation barrier, or the less-stable  $\text{H}_3\text{Si-SiH}$ , which can be formed with at most a small activation barrier. Although little is known about the detailed reaction paths for the hydrogen abstraction reactions noted above, it seems plausible that the  $\text{Si}_2\text{H}_4$  formed by the  $\text{Si}_2\text{H}_5 + \text{F}$  reaction will be the more-stable species ( $\text{H}_2\text{Si-SiH}_2$ ), since the constraints responsible for the barrier to  $\text{H}_2$  loss would not be present here.

The photoion yield curve of  $\text{Si}_2\text{H}_4^+$  ( $\text{Si}_2\text{H}_4$ ) is displayed in Fig. 3(a). From threshold ( $\sim 8.1$  eV) one sees a gradually increasing curve to  $\sim 8.9$  eV. Above  $\sim 8.9$  eV, the photoion yield curve levels off and actually appears to diminish slightly, until  $\sim 9.4$  eV. This latter energy marks the onset of an enhancement in  $\text{Si}_2\text{H}_4^+$  intensity which is approximately linear with energy to 9.9 eV, the limit of the present study. A spline function fitted to this data set is also shown in Fig. 3(a). Magnification of the threshold region by a factor 5 reveals a roughly linear descent to threshold, with a slight change of slope between 8.12 and 8.07 eV, which may be due to a hot band. To encompass this uncertainty, we choose  $8.09 \pm 0.03$  eV as the adiabatic threshold. Figure 3(b) displays the derivative of the spline function. Here, the simulation of the photoelectron spectrum reveals that the first band actually consists of two bands, with vertical ionization potentials at  $\sim 8.24$  and  $\sim 8.73$  eV, while the third band has a vertical ionization potential  $\geq 9.76$  eV. The adiabatic ionization potential of the third band (9.4 eV) is most reliably

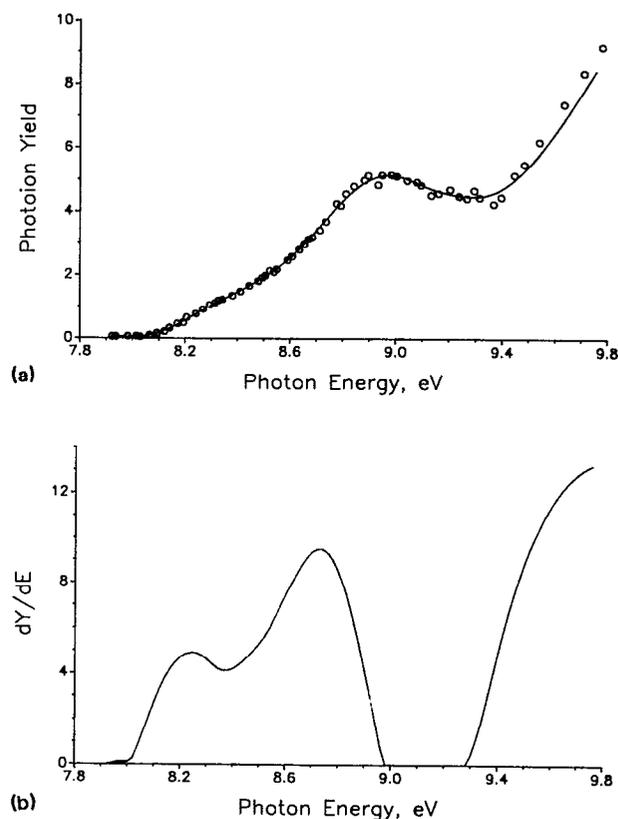


FIG. 3. (a) The photoion yield curve of  $\text{Si}_2\text{H}_4^+$  ( $\text{Si}_2\text{H}_4$ ). The continuous curve is a spline function fitted to the data. (b) The derivative of the fitted curve in (a), simulating the photoelectron spectrum.

extracted from the photoion yield curve itself. The gap between the adiabatic and vertical ionization potentials of the first band ( $\sim 0.15$  eV) is about half that in  $\text{Si}_2\text{H}_5$ , but still indicates some geometry change between the ground states of the neutral species and the cation.

### 2. The $\text{Si}_2\text{H}_2^+$ fragment

During the experiments involving the  $\text{F} + \text{Si}_2\text{H}_6$  reaction, some  $\text{Si}_2\text{H}_2^+$  photoion intensity is observed at lower energies than is observed from  $\text{Si}_2\text{H}_6$  alone (threshold at  $\sim 11.75$  eV). The lowest-energy path for generating  $\text{Si}_2\text{H}_2^+$  under these conditions (apart from  $\text{Si}_2\text{H}_2$  neutral, for which there is evidence; see below) is  $\text{H}_2$  loss from  $\text{Si}_2\text{H}_4^+$ . The photoion yield curve for  $\text{Si}_2\text{H}_2^+$  under these conditions appears in Fig. 4. One observes a weakly increasing signal from  $\leq 8.57$  eV to  $\sim 9.55$  eV, followed by a signal of increased slope to  $\sim 9.9$  eV. As will be shown below, it is also possible to observe  $\text{Si}_2\text{H}_2^+$  from  $\text{Si}_2\text{H}_2$ , under somewhat different experimental conditions. This latter data set, normalized in intensity to that of  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_4$ ), is also shown in Fig. 4. From a comparison of these two data sets, it is clear that the region from 8.6 to 9.2 eV is essentially the same, but that a distinct onset occurs for  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_4$ ) at  $\leq 9.54$  eV (9.62 eV at 0 K). There may also be a much weaker onset at  $\sim 9.3_2$  eV (9.4<sub>0</sub> eV at 0 K).

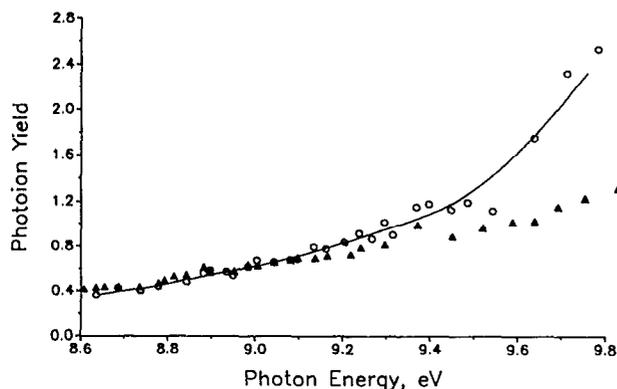
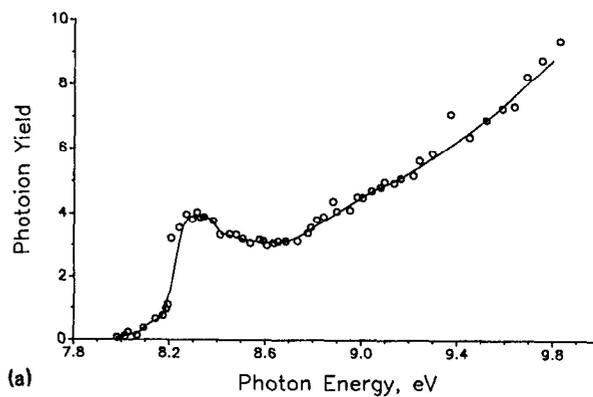


FIG. 4. O, the photoion yield curve of  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_4$ ). The smooth curve is a spline function fitted to the data.  $\blacktriangle$ , a portion of the photoion yield curve of  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_2$ ), which contributes significantly to the  $\text{Si}_2\text{H}_2^+$  signal at low energies.

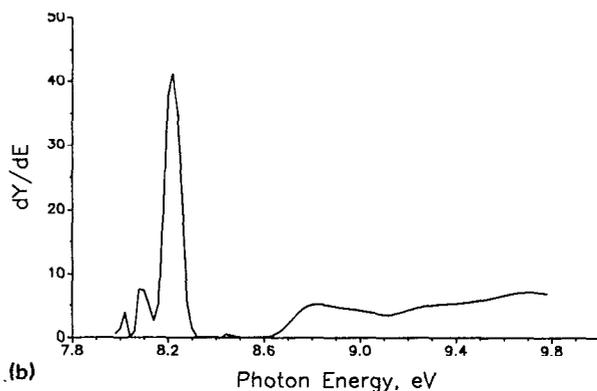
### C. $\text{Si}_2\text{H}_2$

Under certain favorable flow and surface conditions, a significant ion signal above background could be detected for  $\text{Si}_2\text{H}_2^+$  at lower energies than  $\sim 9.5$  eV. We shall demonstrate below that this signal is due to photoionization of the neutral  $\text{Si}_2\text{H}_2$  species. This signal is stronger than that due to  $\text{Si}_2\text{H}_3$  (see below). The  $\text{Si}_2\text{H}_2$  species may be formed on the surfaces of the reaction cell. Each transient species formed has about one chance in five of leaving the cell without a wall collision. Hence the wall collisions are probably not completely destructive. Furthermore, the appearance of the low-energy  $\text{Si}_2\text{H}_2^+$  signal depended upon the past history of the cell. A thin coating of silicon, or a silicon bearing species, may be responsible for the formation of  $\text{Si}_2\text{H}_2$ . White *et al.*<sup>17</sup> have also observed significant surface effects in their kinetics measurements.

In any event, the photoion yield curve of  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_2$ ) is shown in Fig. 5(a). A small bulge appears between 8.10 and 8.20 eV, followed by an abrupt, step-like rise at 8.20 eV, then a plateau until 8.75 eV, beyond which a more-or-less monotonic ascent ensues. In order to fit this experimental curve with optimum fidelity, it was necessary to apply one smoothing function to the abrupt threshold region, and another to the remainder of the curve. These were combined into a single smoothing function, also shown in Fig. 5(a). The derivative of this function appears in Fig. 5(b). As one would expect, the derivative function displays a relatively sharp, intense peak near threshold, with some smaller undulations to lower energy. The most plausible interpretation is that the small undulations near threshold are probably hot bands or possibly experimental scatter, and that the dominant peak represents the 0-0 vibrational component of this transition. In other words, the adiabatic and vertical ionization potentials for this transition are identical, and hence the molecular structure of the ground state of  $\text{Si}_2\text{H}_2$  must be very close to that of  $\text{Si}_2\text{H}_2^+$ . In addition, there appear to be two excited states (or structures) of  $\text{Si}_2\text{H}_2^+$ , both of which are represented by broader bands, signifying some change of geometry in these transitions. The first excited state (or structure) has an adiabatic ionization potential



(a)



(b)

FIG. 5. (a) The photoion yield curve of  $\text{Si}_2\text{H}_2^+$  ( $\text{Si}_2\text{H}_2$ ). Two different polynomial functions are fitted to the data—one for the sharp increase near threshold, another to the more gradually increasing region beyond threshold. (b) The derivatives of the functions in (a), simulating the photoelectron spectrum.

at  $\sim 8.75$  eV, and a vertical value of  $\sim 8.82$  eV; the second band is less well defined.

The adiabatic ionization potential of  $\text{Si}_2\text{H}_2$  is selected to be  $8.20^{+0.01}_{-0.02}$  eV.

### D. $\text{Si}_2\text{H}_3$

This was the weakest of the transient species observed in these experiments, and hence the data points are subject to the largest error bars. The photoion yield curve appears in Fig. 6(a). The lowest-energy point with significant signal occurs at 7.59 eV. The curve increases more or less monotonically to about 7.8 eV, and then remains flat. As before, a smoothing function has been fitted to the data [and shown in Fig. 6(a)]; the derivative of this smoothed function appears in Fig. 6(b). The shape of this derivative is strongly dependent on the degree of smoothing. The low signal level relative to background, partly attributable to the weaker light intensity at these longer wavelengths in our light source, has thwarted our attempts to attain a better "zero level" in the true signal. The best that can be extracted from this data set is that the adiabatic ionization potential of  $\text{Si}_2\text{H}_3$  is  $\leq 7.59$  eV.

All of the experimentally deduced ionization and appearance potentials described in Sec. III are summarized in Table I, and compared with recent *ab initio* calculations by

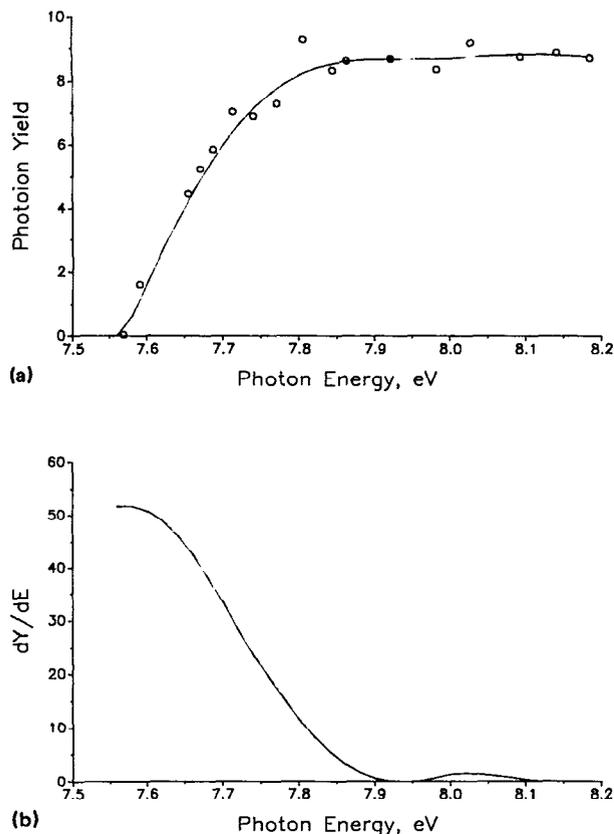


FIG. 6. (a) The photoion yield curve of  $\text{Si}_2\text{H}_3^+$  ( $\text{Si}_2\text{H}_3$ ). The smooth curve is a spline function fitted to the data. (b) The derivative of the fitted curve in (a). In this instance, the degree of smoothing had a significant effect upon the derivative.

Curtiss *et al.*,<sup>14</sup> as well as earlier, crude electron-impact measurements.<sup>25</sup> The *ab initio* calculations are in very good agreement with the photoionization measurements for the ionization potentials of  $\text{Si}_2\text{H}_5$  and  $\text{Si}_2\text{H}_4$ . For  $\text{Si}_2\text{H}_3$ , the calculated value is much lower than our lowest detectable signal. However, the calculated ionization potential for a different structure is very close to our lowest detectable signal. The significance of this observation will become apparent below (Sec. IV B). For  $\text{Si}_2\text{H}_2$ , the calculated value is

TABLE I. Ionization and appearance potentials obtained from photoionization of the transient molecules  $\text{Si}_2\text{H}_5$ ,  $\text{Si}_2\text{H}_4$ ,  $\text{Si}_2\text{H}_3$ , and  $\text{Si}_2\text{H}_2$  (in eV).

	Present results	Robertson and Gallagher <sup>a</sup>	Curtiss <i>et al.</i> <sup>b</sup>
$\text{Si}_2\text{H}_5^+$ ( $\text{Si}_2\text{H}_5$ )	$7.60 \pm 0.05$	7.7	7.64
$\text{Si}_2\text{H}_3^+$ ( $\text{Si}_2\text{H}_3$ )	$< 9.24$ (8.74) <sup>c</sup>	...	8.72
$\text{Si}_2\text{H}_4^+$ ( $\text{Si}_2\text{H}_4$ )	$8.09 \pm 0.03$	7.6	8.11
$\text{Si}_2\text{H}_2^+$ ( $\text{Si}_2\text{H}_2$ )	$< 9.62$ (9.4 <sub>0</sub> ) <sup>c</sup>	...	9.39
$\text{Si}_2\text{H}_3^+$ ( $\text{Si}_2\text{H}_3$ )	$< 7.59$	7.8	6.92
$\text{H}_3\text{SiSi}^+$ ( $\text{H}_3\text{SiSi}$ )			7.57
$\text{Si}_2\text{H}_2^+$ ( $\text{Si}_2\text{H}_2$ )	$8.20 \pm \begin{smallmatrix} 0.01 \\ -0.02 \end{smallmatrix}$	7.7	8.30

<sup>a</sup> Reference 25.

<sup>b</sup> Reference 14.

<sup>c</sup> Probable values, inferred from weak thresholds.

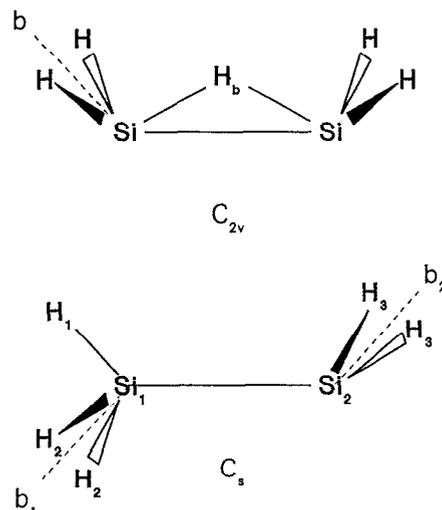
0.10 eV higher than the experimental one. In this case, the experimental onset is abrupt, and appears to be unambiguous.

## IV. INTERPRETATION OF RESULTS

### A. Implications for geometric and electronic structure

#### 1. $\text{Si}_2\text{H}_5$

The shape of the curve in Fig. 1(b) suggests that three cationic states or structures are formed by photoionization of  $\text{Si}_2\text{H}_5$  in the energy interval available for study. All of these cation states (structures) should differ in geometry from neutral  $\text{Si}_2\text{H}_5$ . Ho *et al.*<sup>3</sup> report partial structural information on the neutral species. Köhler and Lischka<sup>26</sup> and also Raghavachari<sup>27</sup> find two stable structures of  $\text{Si}_2\text{H}_5^+$ , which are "isoenergetic within the accuracy of the calculations."<sup>27</sup> One of these (with  $C_s$  symmetry) is very similar to the calculated neutral structure. The other is a bridged ( $C_{2v}$ ) structure. Curtiss *et al.*<sup>14</sup> have recently reexamined these structures, and obtain essentially the same results. The generic shape of these structures is shown below.



The significant geometrical parameters are listed in Table II. However, when comparing structures for detailed geometric features it is best to use a similar level of computational accuracy, preferably from the same group or method of computation, and hence we refer to the structures of Curtiss *et al.*<sup>14</sup> given in Table II.

The major structural change between the neutral and nonbridged cation is the angle of the  $\text{SiH}_2$  group relative to the Si-Si axis. The Si-Si distances differ by about 0.04 Å, and the Si-H distances by about 0.01 Å, neither expected to lead to an extended Franck-Condon vibrational progression.

Curtiss<sup>28</sup> has calculated a vertical ionization potential of 8.29 eV. This value falls between the partially resolved components of the first band in Fig. 1(b), but closer to the second maximum. It suggests that the second maximum corresponds to the  $C_s$  structure of  $\text{Si}_2\text{H}_5^+$ , and the first maximum to the bridged structure. This is counterintuitive, since a transition to the bridged structure is expected to have a broader Franck-Condon range, and hence a larger difference between the adiabatic and vertical I.P. Other interpretations are possible. The differentiation technique may be

TABLE II. Calculated most stable structures of Si<sub>2</sub>H<sub>n</sub> and Si<sub>2</sub>H<sub>n</sub><sup>+</sup> species.

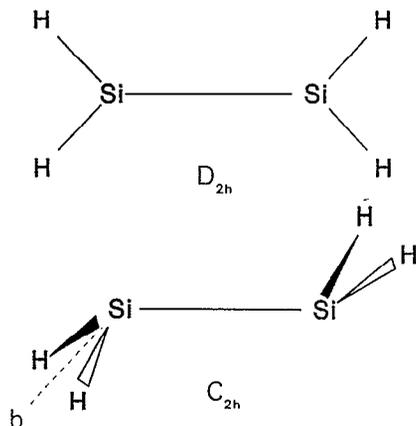
Species	Ho <i>et al.</i> <sup>a</sup>	Kohler and Lischka	Raghavachari	Curtiss <i>et al.</i> <sup>b</sup>	Other		
<b>Si<sub>2</sub>H<sub>5</sub> (C<sub>s</sub>)</b>							
Si-H (Å)	1.479(3) 1.477(2)			1.486(2) 1.488 1.487(2)			
Si-Si (Å)	2.345			2.326			
SiSiH(2) ∠				107.6°			
SiSi <sub>2</sub> ∠				135.3°			
<b>Si<sub>2</sub>H<sub>5</sub><sup>+</sup> (C<sub>s</sub>)</b>							
Si-H (Å)		1.476(2) <sup>c</sup> 1.479 1.482(2)	1.462(2) <sup>d</sup> 1.465 1.463(2)	1.473(2) 1.478 1.475(2)			
Si-Si (Å)		2.496	2.397	2.369			
SiSiH(2) ∠		124.4°		123.9°			
SiSi <sub>2</sub> ∠				178.4°			
<b>Si<sub>2</sub>H<sub>5</sub><sup>+</sup> (C<sub>2v</sub>)</b>							
Si-H (Å)		1.472(4) <sup>c</sup> 1.754	1.456(4) <sup>d</sup> 1.702	1.468(4) 1.698			
Si-Si (Å)		2.231	2.187	2.190			
<b>Si<sub>2</sub>H<sub>4</sub> (C<sub>2h</sub>)</b>							
Si-H (Å)	1.468(4)	1.479(4) <sup>e</sup>	1.47(4) <sup>f</sup>	1.482(4)	1.475(4) <sup>g</sup>	1.48 <sub>5</sub> (4) <sup>h</sup>	
Si-Si (Å)	2.132	2.140	2.13	2.164	2.169	2.22 <sub>4</sub>	
tilt from planarity	0°	3.1°(15.1°) <sup>i</sup>	13°	29°	(29°) <sup>i</sup>	34°	
<b>Si<sub>2</sub>H<sub>4</sub><sup>+</sup> (D<sub>2h</sub>)</b>							
Si-H (Å)			1.46(4) <sup>f</sup>	1.470(4)			
Si-Si (Å)			2.23	2.233			
<b>Si<sub>2</sub>H<sub>2</sub> (C<sub>2v</sub>)</b>							
Si-H (Å)	1.678(4)	1.732 <sup>c</sup>		1.668(4)	(1.679) <sup>i</sup> (4) <sup>j</sup>	1.680(4) <sup>k</sup>	1.668(4) <sup>l</sup>
Si-Si (Å)	2.180	2.246		2.202	2.181	2.194	2.216
HSiH ∠		71.9°		72.9°	(72.5°) <sup>i</sup>	102.6°	72.2°
<b>Si<sub>2</sub>H<sub>2</sub><sup>+</sup> (C<sub>2v</sub>)</b>							
Si-H (Å)			1.68(4) <sup>f</sup>	1.682(4)			
Si-Si (Å)			2.24	2.215			
HSiH ∠				72.3°			
<b>Si<sub>2</sub>H<sub>3</sub> (C<sub>1</sub>)</b>							
Si-H (Å)	1.480 1.478 1.500			1.489 1.485 1.498			
Si-Si (Å)	2.314			2.199			
<b>Si<sub>2</sub>H<sub>3</sub> (C<sub>s</sub>)</b>							
Si-H (Å)				1.490(2) 1.495			
Si-Si (Å)				2.382			
<b>Si<sub>2</sub>H<sub>3</sub><sup>+</sup> (D<sub>3h</sub>)</b>							
Si-H (Å)		1.710 <sup>m</sup>		1.656	1.650 (1.659) <sup>n</sup>		
Si-Si (Å)		2.472		2.368	2.378 (2.373)		

<sup>a</sup> Reference 3.<sup>b</sup> Reference 14.<sup>c</sup> Reference 26.<sup>d</sup> Reference 27.<sup>e</sup> Reference 5.<sup>f</sup> Reference 32.<sup>g</sup> Reference 9.<sup>h</sup> Reference 12.<sup>i</sup> From other parameters given, we calculate the quantity in parentheses.<sup>j</sup> J. S. Binkley, *J. Am. Chem. Soc.* **106**, 603 (1984).<sup>k</sup> J. Kalcher, A. Sax, and G. Olbrich, *Int. J. Quantum Chem.* **25**, 543 (1984).<sup>l</sup> Reference 11.<sup>m</sup> Reference 8.<sup>n</sup> Reference 29.

invalid, if step-function direct ionization is not dominant. The partially resolved first band may be an artifact of the data and the degree of smoothing, although the quality of the data appears to be satisfactory, and the partial resolution occurs over a range of smoothing parameters. Hence, it is conceivable that the partially resolved band is a single, very broad band. Finally, it is possible that the stabilities of the  $C_s$  and  $C_{2v}$  structures of  $\text{Si}_2\text{H}_5^+$  are not as close as given by the *ab initio* calculations. In any event, the high-energy band (maximum at  $\sim 9.25$  eV) must represent a state (or structure) of  $\text{Si}_2\text{H}_5^+$  that has not yet been calculated.

## 2. $\text{Si}_2\text{H}_4$

The three bands seen in Fig. 3(b) also imply transitions to three states (structures) of  $\text{Si}_2\text{H}_4^+$ . *Ab initio* calculations have focused primarily on two structures for both neutral and cation— $\text{H}_2\text{Si}-\text{SiH}_2$  and  $\text{H}_3\text{Si}-\text{SiH}$ . (Other structures have been reported for neutral  $\text{Si}_2\text{H}_4$  by Köhler and Lischka,<sup>5,6,8</sup> but they are significantly higher in energy.) Our assumption here is that successive H-atom abstraction from  $\text{Si}_2\text{H}_6$  will form the more stable  $\text{H}_2\text{Si}-\text{SiH}_2$ . Furthermore, the more stable cation also has the symmetric structure, and Franck–Condon factors connecting  $\text{H}_2\text{Si}-\text{SiH}_2$  with  $\text{H}_3\text{Si}-\text{SiH}^+$  should be significantly weaker, and give rise to a very broad band. Consequently, the structures involved in the ionizing transition near threshold should both be nearly ethylene-like, but the neutral species is calculated to be nonplanar ( $C_{2h}$ ) while the cation is planar ( $D_{2h}$ ). These characteristic shapes are shown below. The detailed geometrical parameters obtained by various authors are collected in Table II.

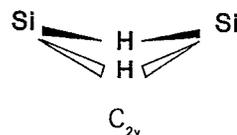


We conclude from this table that the major structural changes occurring upon ionization near threshold include a slight tilt toward planarity and an increase in the Si–Si distance of  $0.08 \pm 0.02$  Å. The first band in Fig. 2(b) appears to be consistent with such a change. The two higher-energy bands, which are more intense, may involve ionization from  $\pi$ -like orbitals. The width and intensity of these bands imply Franck–Condon factors similar to those of the first band. We are unaware of calculations which may have explored the potential-energy surfaces of  $\text{Si}_2\text{H}_4^+$  at these higher energies.

## 3. $\text{Si}_2\text{H}_2$

The photoion yield curve of Fig. 5(a) and the derivative curve of Fig. 5(b) both indicate that the onset of ionization is abrupt, and hence that the ground-state structures of  $\text{Si}_2\text{H}_2$

and  $\text{Si}_2\text{H}_2^+$  are very similar. The *ab initio* calculations bear this out. Both neutral and cation have been found to be bridged, but nonplanar ( $C_{2v}$ ) (see below), with calculated geometrical parameters given in Table II.

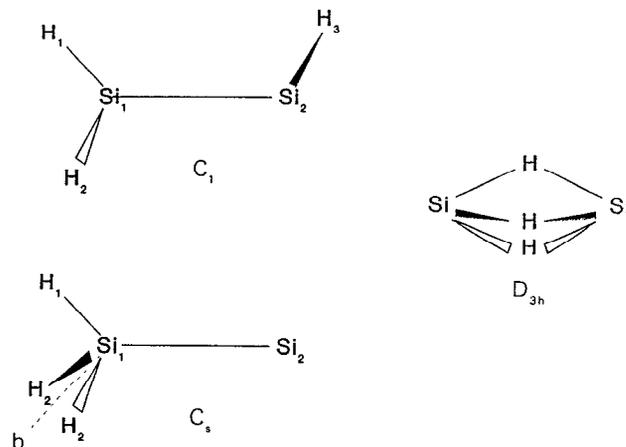


The recent results of Curtiss *et al.*<sup>14</sup> and of Colegrove and Schaefer<sup>11</sup> on  $\text{Si}_2\text{H}_2$ , obtained by somewhat different calculational methods, are in excellent agreement. For the purpose of inferring changes in geometry between  $\text{Si}_2\text{H}_2$  and  $\text{Si}_2\text{H}_2^+$ , we refer to the calculations of Curtiss *et al.*, obtained by a consistent method, at the same level of accuracy. We note that the change in Si–H distance is 0.014 Å, and in the Si–Si distance, 0.013 Å. Also, the dihedral angle remains nearly constant. Hence, within the calculational uncertainty, the two structures are nearly identical.

The broad bands at higher energy provide evidence for excited states (structures) of the cation with geometries substantially different from that of the neutral. Curtiss *et al.*<sup>14</sup> have calculated that the structure  $\text{H}_2\text{SiSi}^+$  lies 0.23 eV above  $\text{Si}(\text{H}_2)\text{Si}^+$ , while  $\text{HSiSiH}^+$  is 0.62 eV higher than the ground state. In addition, Curtiss<sup>28</sup> finds a singly bridged structure, excited by 0.45 eV. The transition to an  $\text{H}_2\text{SiSi}^+$  structure would be expected to have the poorest Franck–Condon factors, and hence such a transition might well escape detection. Either of the other structures (unbridged or singly bridged) could be candidates for the broad feature at  $\sim 8.8$  eV, i.e., about 0.6 eV above the ground state.

## 4. $\text{Si}_2\text{H}_3$

Due to the limitations on this experiment mentioned in Sec. III D, it is difficult to draw conclusions on structural changes. Köhler and Lischka,<sup>8</sup> and more recently Colegrove and Schaefer<sup>29</sup> and Curtiss *et al.*,<sup>14</sup> have concluded that  $\text{Si}_2\text{H}_3^+$  has a symmetric, tribridged structure. Ho *et al.*<sup>3</sup> find an  $\text{HSi}-\text{SiH}_2$  structure for the neutral species, while both Sax and Kalcher<sup>13</sup> and Curtiss *et al.*<sup>14</sup> report that  $\text{Si}-\text{SiH}_3$  is slightly more stable than  $\text{HSi}-\text{SiH}_2$ . These structures are shown schematically below; the significant calculated parameters are entered in Table II.

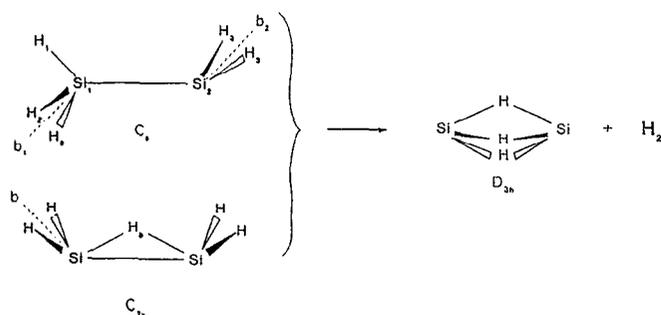


If either of these is the stable neutral species, one would expect very poor Franck–Condon factors near threshold. Colegrove and Schaefer<sup>29</sup> have examined a number of higher-energy structures for  $\text{Si}_2\text{H}_3^+$ . The lowest of these (about 0.5 eV higher than the tribridged structure) are (a) a dibridged structure, and (b) an HSi–SiH<sub>2</sub><sup>+</sup>, or possibly a singly bridged structure. The shape of Figs. 6(a) and 6(b) would not appear to be consistent with a transition of the type HSi–SiH<sub>2</sub> → Si(H<sub>3</sub>)Si<sup>+</sup> which implies a very broad band with very poor Franck–Condon factors. (Such a transition between a singly bridged and a triply bridged structure in B<sub>2</sub>H<sub>5</sub> was found<sup>30</sup> to be orders of magnitude weaker than a favorable transition.) However, it would<sup>30</sup> be consistent with a transition between unbridged, singly bridged, or doubly bridged structures. In other words the  $\text{Si}_2\text{H}_3^+$  signal accessible in our study probably involves a transition from a neutral structure (as yet unclear) to one of the excited structures of  $\text{Si}_2\text{H}_3^+$  lying about 0.5 eV above the tribridged ground state. This, in turn, implies that our lower limit to the adiabatic ionization potential of  $\text{Si}_2\text{H}_3$  is about 0.5 eV too high. Sax and Kalcher,<sup>13</sup> and Curtiss *et al.*,<sup>14</sup> find that the most-stable  $\text{Si}_2\text{H}_3$  structure is SiSiH<sub>3</sub>, but it is calculated to be more stable than HSiSiH<sub>2</sub> by only  $\lesssim 1$  kcal/mol. Hence, on energetic grounds either or both of these isomers may be formed in the F + Si<sub>2</sub>H<sub>6</sub> reaction. Perhaps significantly, Curtiss *et al.*<sup>14</sup> have calculated the ionization potential of SiSiH<sub>3</sub> to SiSiH<sub>3</sub><sup>+</sup> to be 7.57 eV, which is essentially the value of our lowest detectable point (7.59 eV) (See Table I). This observation provides some evidence for the formation of SiSiH<sub>3</sub> in our reaction chamber.

## B. Mechanisms of dissociative ionization from the transient species

### 1. $\text{Si}_2\text{H}_3^+$ from $\text{Si}_2\text{H}_5$

The various *ab initio* calculations are in general agreement regarding the ground-state structures of  $\text{Si}_2\text{H}_5^+$  and  $\text{Si}_2\text{H}_3^+$ . This enables us to speculate about the nature of the transition state(s) involved in the decomposition of  $\text{Si}_2\text{H}_5^+$  to  $\text{Si}_2\text{H}_3^+$  + H<sub>2</sub>. Both Raghavachari<sup>27</sup> and Köhler and Lischka<sup>26</sup> conclude that a singly bridged and a classical structure for  $\text{Si}_2\text{H}_5^+$  are essentially isoenergetic. Both Köhler and Lischka<sup>8</sup> and Colegrove and Schaefer<sup>29</sup> concur that the ground state of  $\text{Si}_2\text{H}_3^+$  is tribridged. Thus, we have



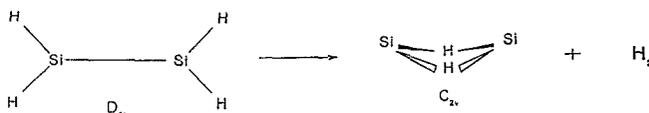
Clearly, the transition state for this reaction must be quite constrained, and the probability of observing this reaction near threshold should be relatively small. However, we have just noted (Sec. IV A 4) that structures have been calculated for  $\text{Si}_2\text{H}_3^+$  which lie about 0.5 eV above the ground state, and are unbridged, dibridged, or possibly singly bridged. The transition states for H<sub>2</sub> loss from  $\text{Si}_2\text{H}_5^+$  to yield one of those excited state structures should be less strained, more comparable to H<sub>2</sub> loss from C<sub>2</sub>H<sub>6</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, or C<sub>2</sub>H<sub>4</sub><sup>+</sup>.

From Figs. 2(a) and 2(b), the strong onset of  $\text{Si}_2\text{H}_3^+$  from  $\text{Si}_2\text{H}_5$  occurs at 9.15 eV by linear extrapolation in Fig. 2(a) (9.24 eV at 0 K). However, there is a weak tail, which appears to have an onset at  $\sim 8.74$  eV. The difference between the weak and strong onset is 0.5 eV, which is tantalizingly close to the difference between our conjectured small and large probabilities of dissociation. Taking  $7.60 \pm 0.05$  eV as the ionization potential of  $\text{Si}_2\text{H}_5^+$ , we can calculate 1.64 eV as the energy for H<sub>2</sub> loss from  $\text{Si}_2\text{H}_5^+$  (strong process), or 1.14 eV for the weak process, all at 0 K. Lischka and Köhler<sup>8</sup> have calculated  $\Delta H_{298} = 18.3$  kcal/mol for this process, equivalent to  $\Delta H_0 = 16.6$  kcal/mol or 0.72 eV, almost 0.5 eV lower still than our lowest possible threshold.

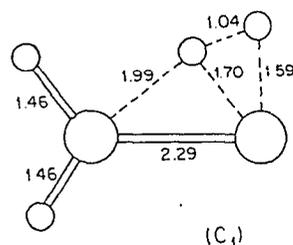
A somewhat less-direct measurement of this decomposition energy may be obtained from the photoionization measurements on  $\text{Si}_2\text{H}_6$ .<sup>22</sup> There, we have determined the appearance potential of  $\text{Si}_2\text{H}_5^+$  ( $\text{Si}_2\text{H}_6$ ) as  $\leq 11.59 \pm 0.02$  eV, and with high probability,  $11.41 \pm 0.03$  eV (both at 0 K). Also, we obtained A.P.  $\text{Si}_2\text{H}_3^+$  ( $\text{Si}_2\text{H}_6$ )  $\leq 13.00 \pm 0.04$  eV, and probably  $\leq 12.70$ . The difference between A.P. ( $\text{Si}_2\text{H}_3^+$ ) and A.P. ( $\text{Si}_2\text{H}_5^+$ ) is 1.29 eV, a measure of H<sub>2</sub> loss from  $\text{Si}_2\text{H}_5^+$  which is comparable to the values obtained directly from an  $\text{Si}_2\text{H}_3$  target. Raghavachari<sup>31</sup> calculated the energy of a transition state for H<sub>2</sub> loss from  $\text{Si}_2\text{H}_5^+$  at 1.43 eV. The nature of the transition state implies that the product  $\text{Si}_2\text{H}_3^+$  may have a single hydrogen bridge, not the triply bridged ground-state structure.

### 2. $\text{Si}_2\text{H}_2^+$ from $\text{Si}_2\text{H}_4$

Raghavachari<sup>32</sup> calculated the ground-state structures of both  $\text{Si}_2\text{H}_4^+$  and  $\text{Si}_2\text{H}_2^+$ . According to these results, the decomposition would take the form



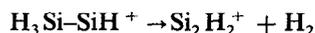
Here again, a severely constrained transition state is implied. According to Raghavachari,<sup>32</sup> this transition state has the structure



It lies 39.2 kcal/mol above H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup>, but the net endothermicity of the decomposition is calculated to be only 24.8 kcal/mol.

The experimental adiabatic ionization potential of Si<sub>2</sub>H<sub>4</sub> (8.09 ± 0.03 eV) appears to be fairly well established from the data of Fig. 3. The appearance potential of Si<sub>2</sub>H<sub>2</sub><sup>+</sup> from Si<sub>2</sub>H<sub>4</sub> (Fig. 4) is not as clear, because of the background attributed to primary ionization of Si<sub>2</sub>H<sub>2</sub>. A distinct onset occurs at <9.62 eV (0 K), but there may be a low-energy tail. Hence, the experimental energy corresponding to H<sub>2</sub> loss from Si<sub>2</sub>H<sub>4</sub><sup>+</sup> is <1.53 eV ≡ 35.3 kcal/mol. This is reasonably close to (0.17 eV lower than) the activation energy calculated for this reaction.

It is also instructive to examine this decomposition process when it originates from the photoionization of Si<sub>2</sub>H<sub>6</sub>. A weak threshold, identified with the H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup> structure, is observed at 10.04 ± 0.02 eV. The stronger onset, attributed to the formation of H<sub>3</sub>Si-SiH<sup>+</sup>, has an extrapolated threshold (0 K) at <10.81 ± 0.02 eV. The corresponding Si<sub>2</sub>H<sub>2</sub><sup>+</sup> threshold occurs at <11.72 ± 0.04 eV. Once H<sub>3</sub>Si-SiH<sup>+</sup> is formed, it can probably rearrange (with an activation energy of 3.8 kcal/mol, according to Raghavachari<sup>32</sup>) to H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup>. It can also form the aforementioned transition state, requiring an activation energy of 27.7 kcal/mol,<sup>32</sup> before decomposing to Si<sub>2</sub>H<sub>2</sub><sup>+</sup> + H<sub>2</sub>. Thus, the reaction



is predicted<sup>32</sup> to have an activation energy of 1.20 eV, and an endothermicity of 13.3 kcal/mol ≡ 0.58 eV. From the difference in appearance potentials forming H<sub>3</sub>Si-SiH<sup>+</sup> and Si<sub>2</sub>H<sub>2</sub><sup>+</sup>, we obtain 0.91 ± 0.04 eV, 0.29 eV lower than the calculated activation energy. Since the transition state for loss of H<sub>2</sub> from H<sub>3</sub>Si-SiH<sup>+</sup> and H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup> is believed to be the same,<sup>32</sup> the two experimental estimates of the energy of the transition state should be the same. According to our interpretation of the present experiments, this is not quite true—the transition state is located 0.17 eV below the calculated one in the H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup> experiment, and 0.29 eV below the calculated one in the H<sub>3</sub>Si-SiH<sup>+</sup> experiment.

## C. Thermochemical implications—heats of formation

### 1. ΔH<sub>f</sub><sup>0</sup>(Si<sub>2</sub>H<sub>4</sub>)

The lowest-energy fragment from Si<sub>2</sub>H<sub>6</sub> is Si<sub>2</sub>H<sub>4</sub><sup>+</sup>, and consequently its appearance potential is expected to be closest to the true thermochemical threshold. It was shown<sup>22</sup> that a weak onset occurs at 10.04 ± 0.02 eV (0 K) and a much stronger growth in signal occurs at 10.81 ± 0.02 eV (0 K). The adiabatic ionization potential reported here for Si<sub>2</sub>H<sub>4</sub> is 8.09 ± 0.03 eV. Combining the lower appearance potential (10.04 eV, attributed to formation of H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup>) and its ionization potential, we obtain for the neutral decom-



the threshold value 1.95 ± 0.03 eV, or 45.0 ± 0.8 kcal/mol at 0 K. This quantity should refer to the formation of Si<sub>2</sub>H<sub>4</sub> in its most-stable state, if we are correct in attributing the weak appearance potential at 10.04 eV to the formation of H<sub>2</sub>Si-SiH<sub>2</sub><sup>+</sup>, and the adiabatic ionization potential measured is that of H<sub>2</sub>Si-SiH<sub>2</sub>.

Before we compare the present experimental endothermicity of reaction (1) with *ab initio* calculations, it is helpful to establish the relationship between various energy quantities at 298 and 0 K. Most of the vibrational frequencies of Si<sub>2</sub>H<sub>6</sub> have been measured.<sup>33</sup> The significant torsional frequency has now been calculated.<sup>9</sup> With this information, one can calculate  $H_{298} - H_0$  for Si<sub>2</sub>H<sub>6</sub>, and also the internal thermal energy  $E_{\text{rot}} + E_{\text{vib}}$  at 298 K, both of which are given in Table III. This internal thermal energy is the quantity used to correct the fragmentation thresholds to 0 K. Utilizing established<sup>34</sup> values of  $H_{298} - H_0$  for H<sub>2</sub> and Si (crystal), one can deduce the difference in heat of formation,  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_6) - \Delta H_{f,0}^0(\text{Si}_2\text{H}_6)$ , which is also given in Table III and compared with corresponding values from other compilations.<sup>35,36</sup> The agreement with the National Bureau of Standards (U.S.) (NBS) compilation is satisfactory.

For Si<sub>2</sub>H<sub>4</sub>, in the absence of experimental data on vibrational frequencies, we have utilized the frequencies calculated by Gordon, Truong, and Bonderson,<sup>9</sup> but reduced by factors determined by comparing their calculated frequencies of Si<sub>2</sub>H<sub>6</sub> with the experimental ones. The heat content and ΔH<sub>f</sub> changes for Si<sub>2</sub>H<sub>4</sub> are also given in Table III. For completeness, we also include the corresponding energy quantities for Si<sub>2</sub>H<sub>5</sub>, Si<sub>2</sub>H<sub>3</sub>, Si<sub>2</sub>H<sub>2</sub>, and Si<sub>2</sub>H, which were obtained by utilizing the corresponding frequencies given by Ho *et al.*<sup>3</sup> and appropriately reduced.

In Table IV, we compare our measured enthalpy for reaction (1) with results from *ab initio* calculations and other experiments. Three of the calculated values are explicitly given for ΔH<sub>298</sub>; the value given by Gordon, Truong, and Bonderson<sup>9</sup> appears to refer to ΔH<sub>0</sub>. One can readily see

TABLE III. Relationship between enthalpies at 298 K and 0 K (kcal/mol).

	$H_{298} - H_0$	Internal energy $\Delta H_{f,0}^0 - \Delta H_{f,298}^0$ at 298 K	
Si <sub>2</sub> H <sub>6</sub>	3.811	2.329	3.800 3.76 <sup>a</sup> 4 <sup>b</sup>
Si <sub>2</sub> H <sub>5</sub>	3.681	2.200	2.916
Si <sub>2</sub> H <sub>4</sub>	3.411	1.930	2.175
Si <sub>2</sub> H <sub>3</sub>	3.286	1.805	1.288
Si <sub>2</sub> H <sub>3</sub> <sup>+</sup> (tribridged)	2.607	1.125	1.967
Si <sub>2</sub> H <sub>2</sub>	2.581	1.100	0.981
Si <sub>2</sub> H	2.757	1.275	-0.207
Si <sub>2</sub>	2.214	0.733	-0.676
Si <sub>2</sub> H <sub>6</sub> → Si <sub>2</sub> H <sub>4</sub> + H <sub>2</sub>			
ΔH <sub>298</sub> - ΔH <sub>0</sub> = 1.625 kcal/mol			

<sup>a</sup> Reference 35.

<sup>b</sup> Reference 36.

TABLE IV. Comparison of experimental and calculational results for the endothermicity of the reaction Si<sub>2</sub>H<sub>6</sub> → Si<sub>2</sub>H<sub>4</sub> + H<sub>2</sub> (in kcal/mol).

	$\Delta H_0$	$\Delta H_{298}$
Experimental		
Present results	45.0 ± 0.8	46.6 ± 0.8
Becerra and Walsh <sup>a</sup>		≤44.0
Olbrich <i>et al.</i> <sup>b</sup>		≤52.1 ± 2.6
White <i>et al.</i> <sup>c</sup>		≤38.8
Calculational		
Curtiss <i>et al.</i> <sup>d</sup>	45.5	47.3
Sax and Kalcher <sup>e</sup>		47.6
Gordon <i>et al.</i> <sup>f</sup>	47.0	
Ho and Melius <sup>g</sup>		43.8
Ho <i>et al.</i> <sup>h</sup>		38.0
Horowitz and Goddard <sup>i</sup>		53.3

<sup>a</sup> Reference 18.<sup>f</sup> Reference 9.<sup>b</sup> Reference 16.<sup>g</sup> Reference 4.<sup>c</sup> Reference 17.<sup>h</sup> Reference 3.<sup>d</sup> Reference 14.<sup>i</sup> Reference 12.<sup>e</sup> Reference 13.

that the experimental value deduced here lies within the range of the *ab initio* calculations, providing support for the structural assumptions (Si<sub>2</sub>H<sub>4</sub>, Si<sub>2</sub>H<sub>4</sub><sup>+</sup>) mentioned, as well as the thresholds inferred. The most recent calculations, by Sax and Kalcher,<sup>13</sup> and by Curtiss *et al.*,<sup>14</sup> are in satisfactory agreement with our experimental value. The previous experimental values are based on kinetic modeling of the reactions ensuing upon pyrolysis of SiH<sub>4</sub> (640–703 K),<sup>17</sup> which inferred  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_4) \leq 58.0$  kcal/mol, or Hg(<sup>3</sup>P<sub>1</sub>) sensitized photolysis of SiH<sub>4</sub>.<sup>16,18</sup> The initial analysis<sup>16</sup> of the Hg sensitized reaction deduced  $\Delta H_{f,298}^0(\text{H}_2\text{Si}-\text{SiH}_2) < 71.2 \pm 2.6$  kcal/mol. This experiment was subsequently remodeled<sup>18</sup> "... with a complex mechanism in which both silylsilylene, SiH<sub>3</sub>SiH, and disilene, H<sub>2</sub>Si=SiH<sub>2</sub>, play a role." The latter analysis yielded  $\Delta H_{f,298}^0(\text{H}_2\text{Si}=\text{SiH}_2) \leq 62.3$  kcal/mol, or  $\leq 63.1$  kcal/mol. If we accept  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_6) = 19.1$  kcal/mol, then  $\Delta H_{f,298}^0$  for reaction (1) becomes  $\leq 38.8$  kcal/mol, from White *et al.*<sup>17</sup> Olbrich *et al.*<sup>16</sup> explicitly give  $\Delta H_{f,298}^0$  for reaction (1),  $\leq 52.1 \pm 2.6$  kcal/mol, and after the remodeling, Becerra and Walsh<sup>18</sup> obtain  $\leq 44.0$  kcal/mol. In these experiments,

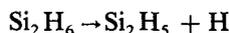
the presence of transient species such as Si<sub>2</sub>H<sub>4</sub> is inferred from the kinetics of formation of stable species (Si<sub>2</sub>H<sub>6</sub>, Si<sub>3</sub>H<sub>8</sub>, etc.), rather than directly detected.

We can convert our value for the enthalpy of reaction (1) into  $\Delta H_{f,298}^0(\text{H}_2\text{Si}-\text{SiH}_2)$  by utilizing the aforementioned  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_6)$ , thus obtaining  $65.7 \pm 0.9$  kcal/mol for this quantity. Other values, based on *ab initio* calculations and kinetics experiments, are listed in Table V. Most of the previous values, both calculational and experimental, are based on  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_6) = 19.1$  kcal/mol, and hence the enthalpy of reaction (1) yields directly  $\Delta H_{f,298}^0(\text{H}_2\text{Si}-\text{SiH}_2)$ . Boatz and Gordon<sup>10</sup> arrive at their value for  $\Delta H_{f,298}^0(\text{H}_2\text{Si}-\text{SiH}_2)$  by calculating (G1 theory) the formation energy of H<sub>2</sub>Si-SiH<sub>2</sub> from 2H<sub>2</sub> + 2Si(g), and then incorporating a literature value for the heat of formation of Si(<sup>3</sup>P). Curtiss *et al.*<sup>14</sup> compute the atomization energy of H<sub>2</sub>Si-SiH<sub>2</sub>, and then utilize "known enthalpies of formation of the isolated atoms," which is tantamount to using a literature value for  $\Delta H_f^0(\text{Si},^3\text{P})$  since  $\Delta H_f^0(\text{H})$  is very well known. Thus, Boatz and Gordon<sup>10</sup> and Curtiss *et al.*<sup>14</sup> ultimately base their value of  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_4)$  on an experimental value for  $\Delta H_{f,298}^0(\text{Si},^3\text{P})$ , whereas the values from the other groups are based on an experimental value for  $\Delta H_{f,298}^0(\text{Si}_2\text{H}_6)$ .

Despite these differences in reference species, the recent *ab initio* calculations<sup>10,13,14</sup> are in very good agreement with the present result. The remodeled Hg sensitized photolysis experiment<sup>18</sup> is the closest experimental value to the present one, but still appears to be low by about 2–3 kcal/mol.

## 2. $\Delta H_f^0(\text{Si}_2\text{H}_5)$

The adiabatic ionization potential of Si<sub>2</sub>H<sub>5</sub> obtained in this study is  $7.60 \pm 0.05$  eV. The appearance potential of Si<sub>2</sub>H<sub>5</sub><sup>+</sup> from Si<sub>2</sub>H<sub>6</sub> deduced previously<sup>31</sup> is  $\leq 11.59 \pm 0.02$  eV (0 K), and probably  $11.41 \pm 0.03$  eV. Hence, we conclude that the bond energy for the reaction



is certainly  $\leq 3.99$  eV ( $11.59 - 7.60$ ), and is probably 3.81 eV ( $11.41 - 7.60$ ) at 0 K. Thus,  $\Delta H_f^0(\text{Si}_2\text{H}_5) \leq 63.3$  kcal/mol, and more probably 59.2 kcal/mol, or at 298 K,  $\leq 60.4$  and 56.3 kcal/mol. These latter values can be com-

TABLE V. Comparison of various determinations for the heat of formation of disilene at 298 K (in kcal/mol).

<i>Ab initio</i> calculations		Experiment	
Ho <i>et al.</i> (1986) <sup>a</sup>	57.1 ± 10	Olbrich <i>et al.</i> (1984) <sup>b</sup>	<71.2 ± 2.6
Horowitz and Goddard (1988) <sup>c</sup>	77.0	White <i>et al.</i> (1985) <sup>d</sup>	≤58.0
Ho and Melius (1990) <sup>e</sup>	62.90 ± 2.30	Becerra and Walsh (1987) <sup>f</sup>	<63.1, <62.3
Boatz and Gordon (1990) <sup>g</sup>	64.9	Present work	65.7 ± 0.9
Sax and Kalcher (1991) <sup>h</sup>	67.1		
Curtiss <i>et al.</i> (1991) <sup>i</sup>	64.5		

<sup>a</sup> Reference 3.<sup>f</sup> Reference 18.<sup>b</sup> Reference 16.<sup>g</sup> Reference 10.<sup>c</sup> Reference 12.<sup>h</sup> Reference 13.<sup>d</sup> Reference 17.<sup>i</sup> Reference 14.<sup>e</sup> Reference 4.

TABLE VI. Comparison of various determinations of  $\Delta H_f^\circ(\text{Si}_2\text{H}_n)$ , in kcal/mol.

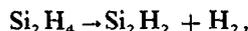
		Ho <i>et al.</i> <sup>a</sup>	Ho and Melius <sup>b</sup>	Horowitz and Goddard <sup>c</sup>	Boatz and Gordon <sup>d</sup>	Sax and Kalcher <sup>e</sup>	Curtiss <i>et al.</i> <sup>f</sup>	Present results
$\text{Si}_2\text{H}_6$	$\Delta H_{f_{298}}^\circ$	$(19.1 \pm 0.3)$	$(19.11 \pm 1.00)$	23.7	...	(19.1)	16.0	$(19.1 \pm 0.3)$
	$\Delta H_f^\circ$	22.9	22.9	27.5	...	22.9	19.8	22.9
$\text{Si}_2\text{H}_5$	$\Delta H_{f_{298}}^\circ$	$55.7 \pm 3$	$55.39 \pm 1.02$	63	...	56.36	53.4	$<60.4$ ; (56.3)
	$\Delta H_f^\circ$	58.7	58.38	66	...	59.35	56.3	$<63.3$ ; (59.2)
$\text{Si}_2\text{H}_4$ ( $^1A_g$ )	$\Delta H_{f_{298}}^\circ$	$57.1 \pm 10$	$62.90 \pm 2.30$	77.0	64.9	67.14; (66.66)	64.5	$65.7 \pm 0.9$
	$\Delta H_f^\circ$	59.3	65.08	79.2	67.1	69.32; (68.84)	66.5	$67.9 \pm 0.9$
$\text{Si}_2\text{H}_3$	$\Delta H_{f_{298}}^\circ$			107				
	$\Delta H_f^\circ$					Si-SiH <sub>3</sub>	98.4; (98.3)	(~95)
	$\Delta H_{f_{298}}^\circ$	$105.8 \pm 3$	$102.05 \pm 2.48$			HSi-SiH <sub>2</sub>	99.7; (99.6)	(~96)
	$\Delta H_f^\circ$	107.1	103.34				99.5; (99.1)	
$\text{Si}_2\text{H}_2$ (cyclic)	$\Delta H_{f_{298}}^\circ$	$89.5 \pm 5$	$95.62 \pm 1.70$			100.8; (100.4)	98.8	
	$\Delta H_f^\circ$	90.5	96.60				91.8	$<99.7$
(acetylenic)	$\Delta H_{f_{298}}^\circ$						92.8	$(89.2-94.6)$
	$\Delta H_f^\circ$					111.1 (110.6)		$<100.7$ (90.2-95.6)
$\text{Si}=\text{SiH}_2$	$\Delta H_{f_{298}}^\circ$	$104.4 \pm 5$	$108.19 \pm 1.94$			112.1 (111.6)		
	$\Delta H_f^\circ$	105.4	109.17			107.9 (106.9)	104.6	
$\text{Si}_2\text{H}$	$\Delta H_{f_{298}}^\circ$	$144.2 \pm 3$	$123.42 \pm 1.55$			108.9 (107.9)	105.2	
	$\Delta H_f^\circ$	144.0	123.21			129.3 (129.0)	127.4	
$\text{SiHSi}$	$\Delta H_{f_{298}}^\circ$	$115.8 \pm 5$	$118.82 \pm 2.86$			129.1 (128.8)	127.2	
	$\Delta H_f^\circ$	115.6	118.61				118.9	
$\text{Si}_2$	$\Delta H_{f_{298}}^\circ$	$(141.0 \pm 3)$ ;	$145.79 \pm 1.31$				118.9	
	$\Delta H_f^\circ$	140.3	145.11			(141.0)	140.3	$(141.0 \pm 3)$ ; $(134.8 \pm 4.5)$
						140.3	139.6	$140.3 \pm 3$ $134.2 \pm 4.5$

<sup>a</sup> Reference 3.<sup>b</sup> Reference 4.<sup>c</sup> Reference 12.<sup>d</sup> Reference 10.<sup>e</sup> Reference 13.<sup>f</sup> Reference 14.

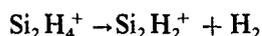
pared with 55.4,<sup>4</sup> 56.4,<sup>13</sup> and 53.4 kcal/mol (Ref. 14) from *ab initio* calculations, and 53.3 (Ref. 37) from an earlier experiment.

### 3. $\Delta H_f^0(\text{Si}_2\text{H}_2)$

An unambiguous value of  $8.20_{-0.02}^{+0.01}$  eV is obtained as the adiabatic ionization potential of Si<sub>2</sub>H<sub>2</sub> in this work. The appearance potential of Si<sub>2</sub>H<sub>2</sub><sup>+</sup> (Si<sub>2</sub>H<sub>4</sub>) is not as clear. There is certainly a strong onset at  $\leq 9.62$  eV (0 K) and possibly a weak one at 9.4<sub>0</sub> eV (0 K). Thus, for the reaction



we infer  $\Delta H_0 < 1.42$  eV, and possibly 1.2 eV. Utilizing our previously obtained value for  $\Delta H_f^0(\text{Si}_2\text{H}_4)$ , which is 67.9 kcal/mol at 0 K, we infer  $\Delta H_f^0(\text{Si}_2\text{H}_2) < 100.7$  kcal/mol, and possibly 95.6 kcal/mol. Raghavachari<sup>32</sup> implicitly calculated a reverse activation energy for the dissociative reaction

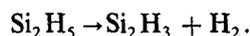


of 14.4 kcal/mol (0.62 eV). If we subtract this quantity from our strong onset, which is then interpreted as the surmounting of an activation barrier, the thermochemical onset becomes 0.8 eV, and  $\Delta H_f^0(\text{Si}_2\text{H}_2) = 86.3$  kcal/mol. However, we had previously (Sec. III B 2) reached the conclusion that Raghavachari's activation energy might be at least 0.17 eV too large. With this interpretation, the thermochemical onset becomes 0.97 eV, and  $\Delta H_f^0(\text{Si}_2\text{H}_2) \sim 90.2$  kcal/mol. Thus, the inference from our experiments is that  $\Delta H_f^0(\text{Si}_2\text{H}_2)$  is definitely  $< 100.7$  kcal/mol, and is probably in the range 90.2–95.6 kcal/mol. Previous *ab initio* calculations for the most-stable structure of Si<sub>2</sub>H<sub>2</sub> are 96.6<sup>4</sup> and 92.8<sup>14</sup> kcal/mol. For the higher-energy H<sub>2</sub>Si=Si structure, calculations yield 109.2,<sup>4</sup> 105.6, and 107.9 (Ref. 13) kcal/mol. To the best of our knowledge, no other experimental values are known.

### 4. $\Delta H_f^0(\text{Si}_2\text{H}_3)$

From our previous analysis (Secs. IV A 4 and IV B 1) neither the adiabatic ionization potential nor the appearance

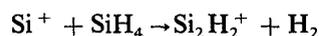
potential of Si<sub>2</sub>H<sub>3</sub><sup>+</sup> from Si<sub>2</sub>H<sub>5</sub> (or Si<sub>2</sub>H<sub>6</sub>) is well established. The appearance potential of Si<sub>2</sub>H<sub>3</sub><sup>+</sup> (Si<sub>2</sub>H<sub>5</sub>) is  $< 9.24$  eV (0 K) and may be as low as 8.74 eV. The adiabatic ionization potential is certainly  $< 7.59$  eV, and may be roughly 0.5 eV lower, according to *ab initio* calculations. From the two clearly observed onsets, we would obtain  $\sim 1.6$  eV for the decomposition reaction



Roughly the same value would be obtained from the lower limits of I. P. and A. P. surmised. Thus, a rough estimate of  $\Delta H_f^0(\text{Si}_2\text{H}_3)$ , based on our determination of  $\Delta H_f^0(\text{Si}_2\text{H}_5) \sim 59.2$  kcal/mol, is  $\sim 96$  kcal/mol at 0 K. Sax and Kalcher<sup>13</sup> obtain 99.7 kcal/mol and Curtiss *et al.*,<sup>14</sup> 98.7 kcal/mol for  $\Delta H_f^0(\text{H}_3\text{Si-Si})$ , which they find more stable than H<sub>2</sub>Si-SiH (using our conversion from  $\Delta H_{f,298}^0$  to  $\Delta H_f^0$ ). For  $\Delta H_f^0(\text{H}_2\text{Si-SiH})$ , calculated values of 100.8,<sup>13</sup> 103.3,<sup>4</sup> and 98.8 (Ref. 14) kcal/mol have been reported.

In Table VI, we summarize the heats of formation of the neutral species obtained in this study, where they are compared with corresponding values obtained by *ab initio* calculations and other experiments. In Table VII, we list the heats of formation of the cations inferred from this work and the preceding paper,<sup>22</sup> and compare them with *ab initio* calculations<sup>14</sup> and experimental values from Boo and Armentrout,<sup>38</sup> where possible. Our values for  $\Delta H_f^0(\text{Si}_2\text{H}^+)$  and  $\Delta H_f^0(\text{Si}_2^+)$  are crude upper limits, and are clearly not as useful as those of Boo and Armentrout. For  $\Delta H_f^0(\text{Si}_2\text{H}_3^+)$ , the two experimental results are comparable. However, for  $\Delta H_f^0(\text{Si}_2\text{H}_2^+)$  the upper limit from Boo and Armentrout is about 20 kcal/mol lower than our most probable value, which we would regard as a lower limit.

Most of the experimental limits in the work of Boo and Armentrout stem from the exothermicity or endothermicity of reactions in which the reactants are Si<sup>+</sup> + SiH<sub>4</sub>. Thus, they find that the reaction



is exothermic. From this observation, they conclude that  $\Delta H_f^0(\text{Si}_2\text{H}_2^+) < 305$  kcal/mol, which is consistent with,

TABLE VII. Heats of formation of Si<sub>2</sub>H<sub>n</sub><sup>+</sup> cations (kcal/mol at 0 K).

	Present results <sup>a</sup>	Boo and Armentrout <sup>b</sup>	Curtiss <i>et al.</i> <sup>c</sup>
Si <sub>2</sub> H <sub>6</sub> <sup>+</sup>	247.5 ± 0.6 <sup>d</sup>		243.5
Si <sub>2</sub> H <sub>5</sub> <sup>+</sup>	<238.5 ± 0.6 <sup>d</sup> (234.4 ± 0.8) <sup>d</sup>		232.5
Si <sub>2</sub> H <sub>4</sub> <sup>+</sup>	254.4 ± 0.6 <sup>d</sup> (H <sub>2</sub> Si-SiH <sub>2</sub> <sup>+</sup> ) <272.2 <sup>d</sup> (H <sub>3</sub> Si-SiH <sup>+</sup> )		253.5 267.1
Si <sub>2</sub> H <sub>3</sub> <sup>+</sup>	<271.1 ± 0.9; <sup>d</sup> <272.2; (260.7) <sup>c</sup>	264.5 (2)	258.5
Si <sub>2</sub> H <sub>2</sub> <sup>+</sup>	<293.1 ± 0.8; <sup>d</sup> <289.7; (284.7) <sup>c</sup>	<265.5 (2.6)	284.2
Si <sub>2</sub> H <sup>+</sup>	<317 <sup>d</sup>	<302.9 (1.6)	306.4
Si <sub>2</sub> <sup>+</sup>	<357 <sup>d</sup>	<326.5 (2)	322.7

<sup>a</sup> Based on  $\Delta H_f^0(\text{Si}_2\text{H}_6) = 22.9 \pm 0.3$  kcal/mol.

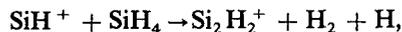
<sup>b</sup> Reference 38. Their values are given for 298 K, using the thermal electron convention. We have corrected them to 0 K.

<sup>c</sup> Reference 14.

<sup>d</sup> Reference 22.

<sup>e</sup> More probable values, deduced from weak onsets.

though higher than our values. Their much lower value comes from their analysis of a different reaction,



for which data are not presented. We believe that their analysis of this reaction may be in error.

By making use of Tables VI and VII, we can compute proton affinities. Thus,  $\text{P.A.}_{298}(\text{Si}_2\text{H}_4) = 365.7 + 65.7 - (231.5) = (199.9)$  kcal/mol. This is almost 40 kcal/mol larger than  $\text{P.A.}(\text{C}_2\text{H}_4) = 162.6$  kcal/mol.<sup>39</sup> Köhler and Lischka<sup>26</sup> have computed  $\text{P.A.}(\text{Si}_2\text{H}_4) = 207$  kcal/mol. Also,  $\text{P.A.}_{298}(\text{Si}_2\text{H}_2) = 365.7 + (92 \pm 3) - (258.7) = (199 \pm 3)$  kcal/mol. The proton affinity of C<sub>2</sub>H<sub>2</sub> is 153.3 kcal/mol,<sup>39</sup> again lower than its silicon analog by almost 50 kcal/mol. Köhler and Lischka<sup>8</sup> have calculated 211 kcal/mol for  $\text{P.A.}(\text{Si}_2\text{H}_2)$ . Curtiss *et al.*<sup>14</sup> obtain  $\text{P.A.}_{298}(\text{Si}_2\text{H}_2) = 201.2$  kcal/mol and  $\text{P.A.}_{298}(\text{Si}_2\text{H}_4) = 200.8$  kcal/mol.

#### D. Thermochemical implications—consecutive Si–H bond energies

From our measured value for reaction (1),  $45.0 \pm 0.8$  kcal/mol, and  $D_0(\text{H}_2) = 103.268$  kcal/mol,<sup>34</sup> we obtain 148.3 kcal/mol for the removal of two H atoms from Si<sub>2</sub>H<sub>6</sub>. We had also concluded that the probable value for removal of one H atom was  $3.81 \text{ eV} \equiv 87.9$  kcal/mol (0 K). Therefore, the Si<sub>2</sub>H<sub>4</sub>–H bond energy is 60.4 kcal/mol at 0 K.

Beyond this point, the accuracy of our determinations will diminish, partly because of cumulative errors and partly because of the presumed difficulty of arriving at true thermochemical thresholds due to the presence of activation barriers. Thus, utilizing  $\Delta H_f^0(\text{Si}_2\text{H}_4) = 67.9 \pm 0.9$  kcal/mol, and the rough estimate for  $\Delta H_f^0(\text{Si}_2\text{H}_3) \cong 96$  kcal/mol, we infer a rough value  $D_0(\text{Si}_2\text{H}_3\text{–H}) \cong 80$  kcal/mol. Introducing

the rough value  $\Delta H_f^0(\text{Si}_2\text{H}_2) = 93 \pm 3$  kcal/mol, we obtain  $D_0(\text{Si}_2\text{H}_2\text{–H}) \cong 49$  kcal/mol. We have no experimental measurement of  $\Delta H_f^0(\text{Si}_2\text{H})$ . Literature values exist for  $\Delta H_f^0(\text{Si}_2)$ , but they are not very precise. Both JANAF (Ref. 34) and the recent NBS tabulation<sup>36</sup> choose  $\Delta H_f^0(\text{Si}_2) = 140.3 \pm 3$  kcal/mol, whereas the Russian compilation<sup>40</sup> selects  $\Delta H_f^0(\text{Si}_2) = 134.2 \pm 4.5$  kcal/mol. Thus, together with our rough value for  $\Delta H_f^0(\text{Si}_2\text{H}_2)$  we compute either  $144.5 \pm 5$  or  $150.6 \pm 4$  kcal/mol for the removal of two H atoms from Si<sub>2</sub>H<sub>2</sub>. Curtiss *et al.*<sup>14</sup> obtain 149.7 kcal/mol for this quantity, whereas the heat of formation of Ho and Melius<sup>4</sup> can be utilized to compute 151.7 kcal/mol. Sax and Kalcher<sup>13</sup> have not calculated the heat of formation of the most-stable (cyclic) Si<sub>2</sub>H<sub>2</sub>, and hence a comparison is not meaningful.

These successive bond energies are summarized in Table VIII. To normalize these values, we divide each bond energy by the average bond energy. In Fig. 7, we plot this fractional bond energy vs the type of bond (M<sub>2</sub>–H, HM<sub>2</sub>–H, etc.) and compare the behavior of the Si<sub>2</sub>H<sub>n</sub> system with current values for the C<sub>2</sub>H<sub>n</sub> system. A similar alternation occurs, as one goes from an even electron to an odd electron system, but the extremes are not as disparate in the Si<sub>2</sub>H<sub>n</sub> system as they are in the C<sub>2</sub>H<sub>n</sub> system.

#### E. Thermochemical implications: Si–Si bond energies

##### 1. $D_0(\text{H}_3\text{Si–SiH}_3)$

In 1962, Steele and Stone<sup>41</sup> obtained 81.3 kcal/mol for this bond energy, from the electron-impact thresholds SiH<sub>3</sub><sup>+</sup>(SiH<sub>4</sub>) and SiH<sub>3</sub><sup>+</sup>(Si<sub>2</sub>H<sub>6</sub>). We can arrive at this value in two different ways. In the preceding paper,<sup>22</sup> we obtain an appearance potential for SiH<sub>3</sub><sup>+</sup>(Si<sub>2</sub>H<sub>6</sub>) of  $\leq 11.72 \pm 0.02$

TABLE VIII. Successive Si–H bond energies for Si<sub>2</sub>H<sub>n</sub> (kcal/mol at 0 K).

	Ho <i>et al.</i> <sup>a</sup> (1986)	Ho and Melius <sup>b</sup> (1990)	Horowitz and Goddard <sup>c</sup> (1988)	Sax and Kalcher <sup>d</sup> (1991)	Curtiss <i>et al.</i> <sup>e</sup> (1991)	Present results
Si <sub>2</sub> H <sub>5</sub> –H	87.4	87.1	90.1	88.1	88.1	87.9
Si <sub>2</sub> H <sub>4</sub> –H	52.2	58.3	64.8	61.5	61.9	60.4
Si <sub>2</sub> H <sub>4</sub> → HSi=SiH <sub>2</sub>	99.4	89.9	...	83.1	83.7	(~80)
HSiSiH <sub>2</sub> → HSi≡SiH	...	...	...	62.9	...	...
HSiSiH <sub>2</sub> → H <sub>2</sub> Si=Si	49.9	57.5	...	63.9 <sup>f</sup>	...	...
HSiSiH <sub>2</sub> → Si(H <sub>2</sub> )Si	35.0	44.9	...	59.5	45.6	(~49)
Si=SiH <sub>2</sub> → Si≡SiH	90.2	65.6	...	60.4 <sup>f</sup>	45.7 <sup>f</sup>	...
HSi≡SiH → Si≡SiH	...	...	...	72.3	...	...
Si(H <sub>2</sub> )Si → Si≡SiH	105.1	78.2	...	68.6	...	...
Si(H <sub>2</sub> )Si → Si(H)Si	76.7	73.6	...	...	77.4	} 149.7 } } 144.5 ± 5* or } 150.6 ± 4
Si <sub>2</sub> –H	76.3	78.1	...	63.0	72.3	

<sup>a</sup> Reference 3.

<sup>b</sup> Reference 4.

<sup>c</sup> Reference 12.

<sup>d</sup> Reference 13. The average value from two basis sets is shown.

<sup>e</sup> Reference 14.

<sup>f</sup> For the Si=SiH<sub>3</sub> structure.

<sup>g</sup> Depending upon the value selected for  $\Delta H_f^0(\text{Si}_2)$ ; see text.

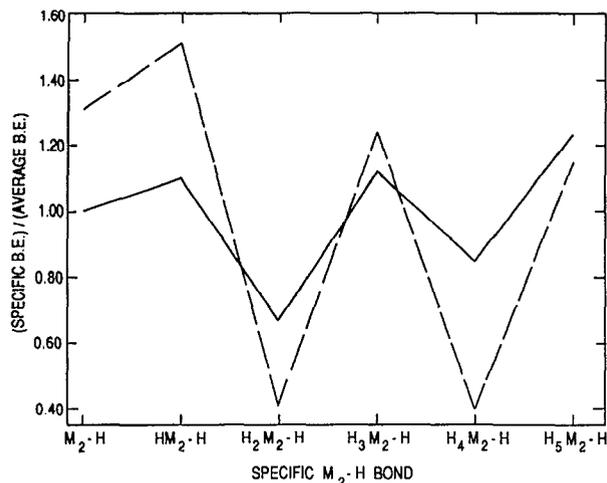


FIG. 7. A plot representing the fraction of the average bond energy represented by successive bonds  $\text{M}_2\text{-H}_n$ , as a function of the particular bond. —,  $\text{M}_2 = \text{Si}_2$ ; ---,  $\text{M}_2 = \text{C}_2$ . The data for  $\text{C}_2\text{H}_n$  are from Refs. 1 and 40. The data for  $\text{Si}_2\text{H}_n$  are from the present work, except  $\text{Si}_2\text{-H}$  and  $\text{HSi}_2\text{-H}$ , which are from Ref. 14.

eV at 0 K. Utilizing I.P. ( $\text{SiH}_3$ ) = 8.135 eV,<sup>24</sup> we obtain  $<3.58_5$  eV  $\cong 82.7$  kcal/mol. Alternatively, from  $\Delta H_f^0(\text{Si}_2\text{H}_6) = 22.9$  kcal/mol and  $\Delta H_f^0(\text{SiH}_3) < 50.0$  kcal/mol,<sup>42</sup> the Si-Si bond energy is  $<77.1$  kcal/mol. It is not surprising that the value based on A.P.  $\text{SiH}_3^+$  ( $\text{Si}_2\text{H}_6$ ) is higher. There are lower-energy processes producing  $\text{Si}_2\text{H}_4^+$ . In the related case of  $\text{CH}_3^+$  from  $\text{C}_2\text{H}_6$ , the appearance potential of  $\text{CH}_3^+$  occurs about 0.4 eV above the thermochemical threshold.<sup>43</sup>

Values based on *ab initio* calculations (see Table IX) are in the range 74–76 kcal/mol at 0 K.

## 2. $D_0(\text{H}_2\text{Si-SiH}_2)$

Our value for this quantity, based on  $\Delta H_f^0(\text{Si}_2\text{H}_4) = 67.9 \pm 0.9$  kcal/mol obtained in the present work, and  $\Delta H_f^0(\text{SiH}_2) = 65.6 \pm 0.7$  kcal/mol reported previously,<sup>44</sup> is  $63.3 \pm 1.2$  kcal/mol. Values determined from *ab initio* calculations vary between  $\sim 59$ – $65$  kcal/mol (see Table IX). In each study,  $D_0(\text{H}_2\text{Si-SiH}_2) < D_0(\text{H}_3\text{Si-SiH}_3)$ , the difference varying from  $\sim 9$ – $17$  kcal/mol. Thus, the nominal Si-Si double bond in  $\text{Si}_2\text{H}_4$  is weaker than the Si-Si single bond in  $\text{Si}_2\text{H}_6$ , an observation which is no longer novel.

TABLE IX. Si-Si bond energies (kcal/mol at 0 K).

	Ho and Melius <sup>a</sup> (1990)	Sax and Kalcher <sup>b</sup> (1991)	Curtiss <i>et al.</i> <sup>c</sup> (1991)	Steele and Stone <sup>d</sup> (1962)	Present work
$D_0(\text{H}_3\text{Si-SiH}_3)$	74.65	75.4 73.7	76.0	81.3	$<82.7$ $<77.1$
$D_0(\text{H}_2\text{Si-SiH}_2)$	65.3	63.8 64.6	58.8	...	$63.3 \pm 1.2$
$D_0(\text{HSi-SiH})$	84.6 <sup>f</sup>	67.0 <sup>e</sup> 67.8 <sup>e</sup>	82.1 <sup>f</sup>	...	$>78.5 \pm 1.7^f$ ( $86.2 \pm 4$ )

<sup>a</sup> Reference 4.

<sup>b</sup> Reference 13.

<sup>c</sup> Reference 14.

<sup>d</sup> Reference 41.

<sup>e</sup>  $\text{HSi}\equiv\text{SiH}$ .

<sup>f</sup> Cyclic  $\text{Si}_2\text{H}_2$ .

## 3. $D_0(\text{Si}_2\text{H}_2)$

First, we must clearly state that this dissociation in our work presumably involves the hydrogen bridged, cyclic  $\text{Si}_2\text{H}_2$  decomposing into two SiH molecules, since the cyclic structure is the most-stable state. From  $\Delta H_f^0(\text{Si}_2\text{H}_2) \cong 93 \pm 3$  kcal/mol (this work) and  $\Delta H_f^0(\text{SiH}) = 89.6 \pm 1.2$  kcal/mol,<sup>23(b)</sup> we infer  $86.2 \pm 4$  kcal/mol for this decomposition. From Ho and Melius,<sup>4</sup> we obtain 84.6 kcal/mol, whereas Curtiss *et al.*<sup>14</sup> find 82.1 kcal/mol. Sax and Kalcher<sup>13</sup> do not calculate the cyclic structure, but they do give a value for the nominally triple bonded  $\text{HSi}\equiv\text{SiH}$ . Their value for dissociation into 2SiH is slightly larger than their  $D_0(\text{H}_2\text{Si-SiH}_2)$ , but distinctly smaller than their  $D_0(\text{H}_3\text{Si-SiH}_3)$ .

Thus, formation of a nominal double or triple Si-Si bond apparently adds little or nothing to the bond strength, while formation of the cyclic structure adds to the bonding between two SiH entities. By contrast  $D_0(\text{H}_3\text{C-CH}_3) = 87.6$  kcal/mol,<sup>40</sup>  $D_0(\text{H}_2\text{C=CH}_2) = 171.9$  kcal/mol,<sup>40</sup> and  $D_0(\text{HC}\equiv\text{CH}) = 229.5$  kcal/mol.<sup>40</sup>

## V. DISCUSSION

The relative bond strengths of successive  $\text{H}_n\text{Si}_2\text{-H}$  bonds illustrated in Fig. 7 are not remarkable. They display an alternation similar to, but not as pronounced as the  $\text{H}_n\text{C}_2\text{-H}$  bonds. From this evidence alone, one would not suspect the dramatic structural changes in  $\text{Si}_2\text{H}_n$  compounds, compared to their carbon counterparts. Our experimental evidence would not suffice to deduce these structural changes. They are gleaned largely from modern *ab initio* calculations. On the other hand, the experimental data are essential in establishing that the lowest-energy structures have been explored by the *ab initio* calculations, and in assessing the relative accuracy of alternative calculations. Structural information is best determined by spectroscopy, and doubtless some of the structures discussed herein will be tested in the near future. Indeed, the technique utilized in the present work to generate  $\text{Si}_2\text{H}_n$  ( $n = 2-5$ ) should be readily adaptable to matrix-isolation spectroscopy. At this time, however, certain structural features seem highly probable. The abrupt onset in the photoionization process  $\text{Si}_2\text{H}_2 \rightarrow \text{Si}_2\text{H}_2^+ + e$  indicates that the structures of neutral and cation are very nearly the same. The fact that *ab initio* calculations predict this similarity, and very nearly the correct ionization poten-

tial (8.20 eV experiment; 8.30 eV calculation<sup>14</sup>) is not likely to be an accident. Hence, the cyclic structure which is consistent with this observation is in all likelihood the correct structure. By contrast, the difficulty in establishing an accurate appearance or ionization potential in forming  $\text{Si}_2\text{H}_3^+$  argues for large structural changes. Photoionization of  $\text{Si}_2\text{H}_6$ ,  $\text{Si}_2\text{H}_5$ , and  $\text{Si}_2\text{H}_4$  reveal changes of an intermediate degree. Even with spectroscopic information, *ab initio* calculations are likely to remain important in predicting transition-state structures.

Considerable attention has been directed at the weak tendency toward multiple bonding for Si, Ge, etc. compared to C. (See, for example, the review articles of Kutzelnigg,<sup>45</sup> and Raabe and Michl<sup>46</sup>). Pauling<sup>47</sup> has focused attention upon the promotion energy from  $s^2p^2$  to  $sp^3$ , and compared this with the energy gained upon forming additional bonds. We present below a simple semiempirical argument similar in principle to an observation by Carter and Goddard<sup>48</sup> which may serve to remove some of the mystery from the apparent paradox presented at the end of Sec. IV E 3.

The dissociation energies of  $\text{B}_2$ ,  $\text{C}_2$ , and  $\text{N}_2$  are<sup>49</sup> 69.6, 143.2, and 225.1 kcal/mol, respectively. These strengths are in the proportion 1:2.06:3.23. They correspond to formation of one  $p\pi$  bond, two  $p\pi$  bonds, and two  $p\pi$  + one  $p\sigma$  bond. Thus, for the first row, a  $p\sigma$  bond is only slightly stronger than a  $p\pi$  bond. We have already mentioned the dissociation energies of  $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$ ,  $\text{C}_2\text{H}_4 \rightarrow 2\text{CH}_2$ , and  $\text{C}_2\text{H}_2 \rightarrow 2\text{CH}$ . For the first two cases, the free radical products in their ground states are also in their "valence states." For the third, the ground state of CH is  $^2\Pi$ , but the "valence state" is  $^4\Sigma^-$ . The promotional energy ( $^2\Pi \rightarrow ^4\Sigma^-$ ) is about<sup>50</sup>  $5844 \text{ cm}^{-1} \equiv 16.7 \text{ kcal/mol}$ . Since two CH products are involved, the dissociation energy of  $\text{C}_2\text{H}_2$  into two  $^4\Sigma^-$  states of CH is 262.9 kcal/mol. The dissociation energies of  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_2$  into their respective products are now in the proportion 1:1.96:3.00. The C-C bond in  $\text{C}_2\text{H}_6$  is formed from  $sp^3$  hybrids, and is a bit stronger than the  $p\sigma$  bond in  $\text{N}_2$ . The  $\pi$  bonds are almost equally strong.

Now let us apply the same approach to the analysis of compounds of the second main row. The dissociation energies of  $\text{Al}_2$ ,  $\text{Si}_2$ , and  $\text{P}_2$  are 35.7, 74.0, and 116.1 kcal/mol.<sup>49</sup> They form the proportions 1:2.07:3.25. They are rough measures of the  $p\pi$  bond in second-row atoms, varying from 35.7 to 38.7 kcal/mol/bond.

The dissociation of  $\text{Si}_2\text{H}_6$  into silyl radicals leaves the latter in ground states which are also valence states. However, the measured dissociation energy of  $\text{Si}_2\text{H}_4$  into two silylene radicals is referred to the ground state ( $^1A_1$ ) of  $\text{SiH}_2$ , which is 21.0 kcal/mol below the valence state ( $^3B_1$ ).<sup>50</sup> When referred to the valence state of  $\text{SiH}_2$ , the dissociation energy of  $\text{Si}_2\text{H}_4$  is  $63.3 + 42.0 = 105.3 \text{ kcal/mol}$ . To continue this argument, we must refer to the triple-bonded  $\text{Si}_2\text{H}_2$ . In Table IX, we note that Sax and Kalcher<sup>13</sup> have computed the dissociation energy from this structure to  $2\text{SiH}$ , and obtain about 67 kcal/mol. The ground state of  $\text{SiH}$  is  $^2\Pi$ . According to Bruna *et al.*,<sup>51</sup> the valence  $^4\Sigma^-$  state is excited by about 36.5 kcal/mol. Therefore, the dissociation energy of  $\text{HSi}\equiv\text{SiH}$  into two  $\text{SiH}$  ( $^4\Sigma^-$ ) entities is  $67 + 73 = 140 \text{ kcal/mol}$ . The dissociation energies of

$\text{Si}_2\text{H}_6$ ,  $\text{Si}_2\text{H}_4$ , and  $\text{HSi}\equiv\text{SiH}$  into their respective valence-state products are now in the proportion 1:1.39:1.84, far from 1:2:3. However, the incremental Si-Si bond energy between disilane and disilene is  $\sim 29 \text{ kcal/mol}$ ; that between disilene and disilyne is  $\sim 35$ . These last two quantities are rough measurements of the  $p\pi$  bonding in Si-Si bonds, and are relatively close to the  $p\pi$  bonding we noted in  $\text{Al}_2$ ,  $\text{Si}_2$ , and  $\text{P}_2$ . This  $p\pi$  bond is much weaker than the  $sp^3$  single bond in  $\text{H}_3\text{Si-SiH}_3$ . In summary, when care is taken to refer the dissociation to valence-state products, the double and triple Si-Si bonds are not weaker than the single bond, as it appeared at first sight. However, the  $p\pi$  bond is nevertheless weak (of order 30-35 kcal/mol). This weakness provides opportunities for other structures to compete successfully. Thus, the cyclic structure of  $\text{Si}_2\text{H}_2$  is  $\sim 15 \text{ kcal/mol}$  more stable than  $\text{HSi}\equiv\text{SiH}$ . The stable structure of  $\text{Ge}_2\text{H}_2$  also appears to be cyclic.<sup>52</sup> In the simple analysis given above,  $\text{Si}_2\text{H}_4$  was implicitly assumed to have an ethylene-like ( $D_{2h}$ ) structure. In fact, numerous *ab initio* calculations (Table II lists the more recent ones) have concluded that  $\text{Si}_2\text{H}_4$  has a nonplanar ( $C_{2h}$ ) structure, with the two  $\text{SiH}_2$  moieties in a *trans*-bent arrangement. From such a geometry, one cannot infer a " $\pi$ -bond energy." However, the difference in potential energy between the  $C_{2h}$  structure and the  $D_{2h}$  structure is very small. This is graphically displayed by Fjeldberg *et al.*<sup>53</sup> Since the  $D_{2h}$  structure can be described as having a  $\sigma + \pi$  bond, the basis for our estimate of a  $\pi$  bond energy for this species has some justification. Indeed, it is the weakness of this  $\pi$  bond that enables the  $C_{2h}$  structure to compete successfully. This behavior is exacerbated in the case of  $\text{Ge}_2\text{H}_4$ , where the planar ( $D_{2h}$ ) structure now represents the barrier in a distinct double-minimum potential.<sup>53-56</sup>

The single-bond energy, as measured by the C-C bond in ethane, the Si-Si bond in disilane, and the Ge-Ge bond in digermane,<sup>57</sup> diminishes monotonically and rather smoothly, from 87.6 to  $\sim 76$  to  $\sim 66 \text{ kcal/mol}$ , respectively. However, the  $\pi$  bond energy, as estimated by taking the weighted average of ( $\text{B}_2$ ,  $\text{C}_2$ ,  $\text{N}_2$ ), ( $\text{Al}_2$ ,  $\text{Si}_2$ ,  $\text{P}_2$ ), [ $\text{Ga}_2$ ,<sup>49</sup>  $\text{Ge}_2$ ,<sup>49</sup>  $\text{As}_2$  (Ref. 49)], and [ $\text{In}_2$ ,<sup>57</sup>  $\text{Sn}_2$ ,<sup>49</sup>  $\text{Sb}_2$  (Ref. 49)], drops precipitately from 73.0 kcal/mol to 37.6, 31.4, and 23.4 kcal/mol for the second, third, and fourth row, respectively.<sup>58</sup> Several reasons have been preferred for this sudden change between first and second row. Kutzelnigg<sup>45</sup> focused attention on lone pair repulsions and isovalent hybridization. The first row has no core  $p$  orbitals, and hence there is no core repulsion from this source. Hybridization is more facile for first-row elements, because the  $2s$  and  $2p$  orbitals are more nearly equal in energy and radial extent. In addition, the electronegativities<sup>59</sup> of H, C, Si, Ge, Sn are 2.1, 2.5, 1.8, 1.8, 1.8. Thus, some additional electron density is available for  $p\pi$  overlap in C-C bonding, whereas some diminution in electron density occurs for rows 2-4. This effect manifests itself in the crystalline solids as well. Thus, the diamond ( $sp^3$  hybrid) and graphite ( $\pi$ -bonded hexagonal network) allotropes of carbon are almost equally stable. In fact, graphite is more stable by  $0.44 \pm 0.04 \text{ kcal/mol}$ .<sup>40</sup> However, for Si,<sup>59</sup> and Ge,<sup>55</sup> the stable crystal structures are cubic, i.e., diamond-like, implying that the  $sp^3$  hybrid is significantly more stable.

With Sn, the gray form (diamond-like) is practically equal in stability to the white form (tetragonal). This marks the onset of metallic behavior, more evident in Pb.

Our familiar view of single, double, and triple bonds, and, in general, electron-pair bonds, is largely based upon extensive studies of carbon compounds and other first-row compounds. Boron was accepted as a rarity, with its tendency to form three-center bonds. We had recently<sup>30</sup> taken note of B<sub>2</sub>H<sub>5</sub><sup>+</sup>, which apparently forms a triple hydrogen bridge. Now, we believe that Si<sub>2</sub>H<sub>3</sub><sup>+</sup> (and perhaps Ge<sub>2</sub>H<sub>3</sub><sup>+</sup>) also form triple hydrogen bridges. Some carbo-cations<sup>1</sup> (C<sub>2</sub>H<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>) have been shown to have ground states with a hydrogen bridge. It is possible that many transient species formed from elements below the first row may be bonded in this fashion, which could influence our traditional view of chemical bonding.

## VI. CONCLUSION

The transient species Si<sub>2</sub>H<sub>5</sub>, Si<sub>2</sub>H<sub>4</sub>, Si<sub>2</sub>H<sub>3</sub>, and Si<sub>2</sub>H<sub>2</sub> have been prepared by reaction of F atoms with Si<sub>2</sub>H<sub>6</sub>, and studied by photoionization mass spectrometry. The adiabatic ionization potentials obtained are Si<sub>2</sub>H<sub>5</sub>, 7.60 ± 0.05 eV; Si<sub>2</sub>H<sub>4</sub>, 8.09 ± 0.03 eV; Si<sub>2</sub>H<sub>3</sub>, <7.59 eV; and Si<sub>2</sub>H<sub>2</sub>, 8.20<sup>+0.01</sup><sub>-0.02</sub> eV. In addition, two fragment appearance potentials were measured: Si<sub>2</sub>H<sub>3</sub><sup>+</sup> (Si<sub>2</sub>H<sub>5</sub>), <9.24 eV (8.74 eV); and Si<sub>2</sub>H<sub>2</sub><sup>+</sup> (Si<sub>2</sub>H<sub>4</sub><sup>+</sup>), <9.62 eV (<9.40 eV), where the parentheses designate probable lower values. By combining these ionization potentials with appearance potentials obtained here and from Si<sub>2</sub>H<sub>6</sub>,<sup>31</sup> the following heats of formation (kcal/mol at 0 K) have been inferred: Si<sub>2</sub>H<sub>5</sub>, <63.3 (59.2); Si<sub>2</sub>H<sub>4</sub>, 67.9 ± 0.9; Si<sub>2</sub>H<sub>3</sub>, (~96); Si<sub>2</sub>H<sub>2</sub>, <100.7 (90.2–95.6). The quantities in parentheses are less well defined. These values are in good agreement with several recent *ab initio* calculations. In particular, Δ*H*<sub>f</sub><sup>0</sup>(Si<sub>2</sub>H<sub>2</sub>), I.P.(Si<sub>2</sub>H<sub>2</sub>), and the shape of the photoion yield curve support the cyclic structure for this neutral species and its cation. Other structures and structural changes resulting from photoionization and dissociative photoionization are discussed. The π bond energy in Al–Al, Si–Si, and P–P is inferred to be ~30–35 kcal/mol, rationalizing the apparent reduction in Si–Si bond strength between disilane and disilene, and providing an explanation for a preference in Si<sub>2</sub>H<sub>2</sub> for a cyclic structure over the triple-bonded structure, and in Si<sub>2</sub>H<sub>4</sub>, a nonplanar (C<sub>2h</sub>) over the planar (D<sub>2h</sub>) structure. It appears that silicon–hydrogen bonding is the typical one for group IV compounds, and the customary view known from carbon–hydrogen bonding is the exception, a view advanced earlier by Kutzelnigg.<sup>45</sup> Heats of formation of cations are also obtained, from which the proton affinities of Si<sub>2</sub>H<sub>2</sub> (199 ± 3 kcal/mol) and Si<sub>2</sub>H<sub>4</sub> (199.9 kcal/mol) are deduced.

## ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

*Note added.* After this paper was submitted, a recent submillimeter wave spectrum of Si<sub>2</sub>H<sub>2</sub> obtained by Bogey *et*

*al.*<sup>60</sup> came to our attention. They obtained an *r*<sub>0</sub> structure very close to those calculated by Curtiss *et al.*<sup>14</sup> and by Colegrove and Schaefer,<sup>11</sup> i.e., puckered ring (C<sub>2v</sub>) with *r*<sub>0</sub>(Si–Si) = 2.2079 Å, *r*<sub>0</sub>(Si–H) = 1.6839 Å, and HSiH angle = 72.56°.

- <sup>1</sup> (a) For C<sub>2</sub>H<sub>5</sub>, see B. Ruscic, J. Berkowitz, L. A. Curtiss, and J. A. Pople, *J. Chem. Phys.* **91**, 114 (1989), and references therein. (b) For C<sub>2</sub>H<sub>3</sub>, see J. Berkowitz, C. A. Mayhew, and B. Ruscic, *J. Chem. Phys.* **88**, 7396 (1988); K. M. Ervin, S. Gronert, S. E. Barlow, M. K. Giles, A. G. Harrison, V. M. Bierbaum, C. H. DePuy, W. C. Lineberger, and G. B. Ellison, *J. Am. Chem. Soc.* **112**, 5750 (1990); A. M. Wodtke, E. J. Hints, J. Somorjai, and Y. T. Lee, *Isr. J. Chem.* **29**, 383 (1989); J. J. Russell, S. M. Senkan, J. A. Saetula, and D. Gutman, *J. Phys. Chem.* **93**, 5184 (1989), and references therein. (c) For C<sub>2</sub>H, see B. Ruscic and J. Berkowitz, *J. Chem. Phys.* **93**, 5586 (1990); and also K. M. Ervin *et al.* [Ref. 1(b)], and references therein.
- <sup>2</sup> S. R. Gunn and L. G. Green, *J. Phys. Chem.* **65**, 779 (1961).
- <sup>3</sup> P. Ho, M. E. Coltrin, J. S. Binkley, and C. F. Melius, *J. Phys. Chem.* **90**, 3399 (1986).
- <sup>4</sup> P. Ho and C. F. Melius, *J. Phys. Chem.* **94**, 5120 (1990).
- <sup>5</sup> H. Lischka and H.-J. Köhler, *Chem. Phys. Lett.* **85**, 467 (1982).
- <sup>6</sup> H. J. Köhler and H. Lischka, *J. Am. Chem. Soc.* **104**, 5884 (1982).
- <sup>7</sup> H. Lischka and H.-J. Köhler, *J. Am. Chem. Soc.* **105**, 6646 (1983).
- <sup>8</sup> H.-J. Köhler and H. Lischka, *Chem. Phys. Lett.* **112**, 33 (1984).
- <sup>9</sup> M. S. Gordon, T. N. Truong, and E. K. Bonderson, *J. Am. Chem. Soc.* **108**, 421 (1986).
- <sup>10</sup> J. A. Boatz and M. S. Gordon, *J. Phys. Chem.* **94**, 7331 (1990).
- <sup>11</sup> B. T. Colegrove and H. F. Schaefer III, *J. Phys. Chem.* **94**, 5593 (1990).
- <sup>12</sup> D. S. Horowitz and W. A. Goddard III, *J. Mol. Struct.* **163**, 207 (1988).
- <sup>13</sup> A. F. Sax and J. Kalcher, *J. Phys. Chem.* **95**, 1768 (1991).
- <sup>14</sup> L. A. Curtiss, K. Raghavachari, P. W. Deutsch, and J. A. Pople, *J. Chem. Phys.* **95**, 1768 (1991).
- <sup>15</sup> G. Olbrich, *Chem. Phys. Lett.* **130**, 115 (1986).
- <sup>16</sup> G. Olbrich, P. Potzinger, B. Reimann, and R. Walsh, *Organometallics* **3**, 1267 (1984).
- <sup>17</sup> R. T. White, R. L. Espino-Rios, D. S. Rogers, M. A. Ring, and H. E. O'Neal, *Int. J. Chem. Kin.* **17**, 1029 (1985).
- <sup>18</sup> R. Becerra and R. Walsh, *J. Phys. Chem.* **91**, 5765 (1987).
- <sup>19</sup> R. Walsh, in *Thermochemistry*, edited by S. Patai and Z. Rappoport (Wiley, New York, 1988), Chap. 5.
- <sup>20</sup> See, for example, J. Berkowitz, *Photoabsorption, Photoionization and Photoelectron Spectroscopy* (Academic, New York, 1979), pp. 291–301.
- <sup>21</sup> J. Berkowitz, C. A. Mayhew, and B. Ruscic, *J. Chem. Phys.* **88**, 7396 (1988).
- <sup>22</sup> B. Ruscic and J. Berkowitz, preceding paper, *J. Chem. Phys.* **95**, 2407 (1991).
- <sup>23</sup> (a) S. T. Gibson, J. P. Greene, and J. Berkowitz, *J. Chem. Phys.* **83**, 4319 (1985); (b) J. Berkowitz, J. P. Greene, H. Cho, and B. Ruscic, *ibid.* **86**, 1235 (1987).
- <sup>24</sup> R. D. Johnson III, B. P. Tsai, and J. W. Hudgens, *J. Chem. Phys.* **91**, 3340 (1989).
- <sup>25</sup> R. Robertson and A. Gallagher, *J. Appl. Phys.* **59**, 3402 (1986).
- <sup>26</sup> H.-J. Köhler and H. Lischka, *Chem. Phys. Lett.* **98**, 454 (1983).
- <sup>27</sup> K. Raghavachari, *J. Chem. Phys.* **92**, 452 (1990).
- <sup>28</sup> L. A. Curtiss (private communication).
- <sup>29</sup> B. T. Colegrove and H. F. Schaefer III, *J. Chem. Phys.* **93**, 7230 (1990).
- <sup>30</sup> B. Ruscic, M. Schwarz, and J. Berkowitz, *J. Chem. Phys.* **91**, 4183 (1989).
- <sup>31</sup> K. Raghavachari (private communication).
- <sup>32</sup> K. Raghavachari, *J. Chem. Phys.* **88**, 1688 (1988).
- <sup>33</sup> G. W. Bethke and E. B. Wilson, *J. Chem. Phys.* **16**, 1107 (1951).
- <sup>34</sup> M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **14**, 1260 (1985); **14**, 1798 (1985).
- <sup>35</sup> D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. Nuttall, *J. Phys. Chem. Ref. Data* **2**, 111 (1982).
- <sup>36</sup> S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Data* **17**, 623 (1988).
- <sup>37</sup> A. M. Doncaster and R. Walsh, unpublished results cited in Ref. 3.
- <sup>38</sup> B. H. Boo and P. B. Armentrout, *J. Am. Chem. Soc.* **109**, 3549 (1987).
- <sup>39</sup> S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data* **13**,

784 (1984).

<sup>40</sup>V. P. Glushko, L. V. Gurvich, G. A. Bergman, I. V. Veits, V. A. Medvedev, G. A. Khachkuruzov, and V. S. Jungman, *Termodinamicheskie Svoistva Individual'nykh Veshchestv* (Nauka, Moscow, 1979), Vol. II.

<sup>41</sup>W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.* **84**, 3599 (1962).

<sup>42</sup>This value for  $\Delta H_f^\circ(\text{SiH}_3)$  is derived from an upper limit to the appearance potential of  $\text{SiH}_3^+$  ( $\text{SiH}_4$ ) given in Ref. 23(b), and the ionization of  $\text{SiH}_3$  from Ref. 24. See also J. Berkowitz, *Acc. Chem. Res.* **22**, 413 (1989).

<sup>43</sup>See J. Berkowitz, Ref. 20, p. 299.

<sup>44</sup>Two alternative values for  $\Delta H_f^\circ(\text{SiH}_2)$  were given in Ref. 23(b), depending upon the choice of I.P. ( $\text{SiH}_2$ ). Subsequent work has favored the lower value,  $65.6 \pm 0.7$  kcal/mol.

<sup>45</sup>W. Kutzelnigg, *Angew. Chem. Int. Ed. Engl.* **23**, 272 (1984).

<sup>46</sup>G. Raabe and J. Michl, *Chem. Rev.* **85**, 419 (1985).

<sup>47</sup>L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.* **80**, 3871 (1983).

<sup>48</sup>E. A. Carter and W. A. Goddard III, *J. Phys. Chem.* **90**, 998 (1986).

<sup>49</sup>K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

<sup>50</sup>See, for example, Ref. 23(b); K. Balasubramanian and A. D. McLean, *J. Chem. Phys.* **85**, (1986); C. W. Bauschlicher, Jr. and S. R. Langhoff, *ibid.* **87**, 387 (1987).

<sup>51</sup>P. J. Bruna, G. Hirsch, R. J. Buenker, and S. D. Peyerimhoff, in *Molecular Ions—Geometric and Electronic Structures*, edited by J. Berkowitz and K.-O. Groeneveld, *Proceeding of the NATO Advanced Studies Institute* (Plenum, New York, (1983), p. 329.

<sup>52</sup>R. S. Grev, B. J. DeLeeuw, and H. F. Schaefer III, *Chem. Phys. Lett.* **165**, 257 (1990).

<sup>53</sup>T. Fjeldberg, A. Haaland, M. F. Lappert, B. E. R. Schilling, R. Seip, and A. J. Thorne, *J. Chem. Soc. Chem. Commun.* **1982**, 1407; D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T. Fjeldberg, A. Haaland, and B. E. R. Schilling, *J. Chem. Soc. Dalton Trans.* **1986**, 2387.

<sup>54</sup>G. Trinquier, J.-P. Malrieu, and P. Riviere, *J. Am. Chem. Soc.* **104**, 4529 (1982).

<sup>55</sup>S. Nagase and T. Kudo, *J. Mol. Struct.* **103**, 35 (1983).

<sup>56</sup>R. S. Grev, H. F. Schaefer III, and K. M. Baines, *J. Am. Chem. Soc.* **112**, 9458 (1990).

<sup>57</sup>The value of  $D_0(\text{H}_3\text{Ge-GeH}_3)$  was estimated by taking the experimental value (Ref. 2) of  $\Delta H_{f,298}^\circ(\text{Ge}_2\text{H}_6) = 38.7 \pm 0.3$  kcal/mol, estimating  $\Delta H_f^\circ - \Delta H_{f,298}^\circ = 3.9$  kcal/mol [thus  $\Delta H_f^\circ(\text{Ge}_2\text{H}_6) = 42.6$  kcal/mol] and  $\Delta H_f^\circ(\text{GeH}_3) = 54.7 \pm 2$  kcal/mol from B. Ruscic, M. Schwarz, and J. Berkowitz, *J. Chem. Phys.* **92**, 1865 (1990).

<sup>58</sup>Various methods have been utilized to estimate  $\pi$ -bond energies. One is given in Ref. 47. Another is given by M. W. Schmidt, P. N. Truong, and M. S. Gordon, *J. Am. Chem. Soc.* **109**, 5217 (1987). The latter examine differences in  $\pi$ -bond energies within a row, as well as between rows. Our estimate is an average for a given row.

<sup>59</sup>L. Pauling, *The Nature of the Chemical Bond* (Cornell University, Ithaca, NY, 1960), pp. 93, 244, and 401–402.

<sup>60</sup>M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes, *Phys. Rev. Lett.* **66**, 413 (1991).