Photoionization studies of GeH$_n$ ($n=2$–$4$)

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(Received 22 August 1989; accepted 9 October 1989)

The adiabatic ionization potential of GeH$_n$ (GeH$_4$) is measured by photoionization mass spectrometry to be $<10.53$ eV and perhaps as low as $10.44$ eV. This is about $0.8$ eV ($\approx 9$ vibrational quanta) lower than the value reported by photoelectron spectroscopy. This result, analogous to that found for SiH$_n^+$ (SiH$_4$), implies a marked Jahn–Teller distortion of GeH$_4^+$. The appearance potentials of GeH$_2^+$ and GeH$_3^+$ from GeH$_4$ are $<10.77 \pm 0.009$ eV and $<11.65 \pm 0.01$ eV, respectively. The reaction of F atoms with GeH$_4$ generates GeH$_3$, GeH$_2$, and some atomic germanium. The adiabatic ionization potential of GeH$_3$ is $<7.94 \pm 0.05$ eV; that of GeH$_2$ is $<9.25$ eV. Together with auxiliary information, limits (more probable values) of the incremental bond energies, in kcal/mol, are found to be $D_0$ (H$_2$Ge–H) $<85.5$ (82 $\pm$ 2); $D_0$ (H$_2$Ge–H) $>56.4$ (59); $D_0$ (HGe–H) $<68.9$ (66); and $D_0$ (Ge–H) $>53.7$ (63). These specific bond energies, when appropriately normalized, display the same pattern as the SiH$_n$ (but not the CH$_n$) bond energies and provide a basis for estimating the corresponding SnH$_n$ bond energies.

I. INTRODUCTION

The paucity of experimental data on the bond strengths in the GeH$_n$ system is astonishing, in view of the extensive use of GeH$_4$ in the semiconductor industry. Increased activity in recent years has clarified the thermochemistry of the corresponding SiH$_n$ system$^1$ and the bond strengths in methane are rather well known.$^{2,3}$ However, in germane the available experimental data are limited to the GeH$_n$–H bond energy$^{4-7}$ and an upper limit to $D_0$ (GeH).$^8$ Even these values are not well established. The more recent results for the bond energy of GeH$_2$–H are $78.0 \pm 1.0$ kcal/mol$^4$ and $83 \pm 2.4$ kcal/mol.$^5$ Earlier values are $<92.3 \pm 4.6$ kcal/mol$^6$ and $87.2$ kcal/mol.$^7$ The upper limit for $D_0$ (GeH) ($<3.3$ eV),$^8$ based on an observed predissociation$^9$ in the $A^2\Delta$ state is not a very useful upper limit, since $D_0$ (SiH) is $2.98 \pm 0.03$ eV$^1$ and one would expect $D_0$ (GeH) to be less than $D_0$ (SiH).

By contrast, accurate ab initio calculations, long limited to first and second row elements, have recently been applied to various aspects of the GeH$_n$ problem. Balasubramanian and Li$^{10}$ have calculated the potential energy curves of several states of GeH, using multiconfiguration self-consistent field (MCSCF) with second-order configuration interaction (CI) and relativistic CI. They obtain $D_0$ (GeH) = 2.81 eV and recommend $D_n$ = 2.85 $\pm$ 0.05 eV, based on comparison of their calculations with other experimentally established values. These numbers are equivalent to $D_0$ (GeH) = 2.70 or 2.74 $\pm$ 0.05 eV, well below the upper limit (3.3 eV) deduced spectroscopically.

Several papers$^{11-14}$ have focused their attention on the $X^1A_1^a$–$A^2B_1$ splitting in GeH$_3$, with calculated values ranging from 19.1 to $\approx 25$ kcal/mol. The more recent separations obtained are 22.8$^{12}$ and 23.8$^{11}$ kcal/mol, slightly higher than in SiH$_2$, but no heats of formation or bond energies have been forthcoming from these calculations.

Within the past year, Kudo and Nagase$^{15}$ have calculated the most stable structure of GeH$_4^+$ and the minimum energy for decomposition of this parent ion into GeH$_2^+ + \text{H}_2$ and GeH$_3^+ + \text{H}$. Their calculations (MP4SDTQ/DZP + ZPC, fourth order Möller–Plesset perturbation theory including single, double, triple, and quadruple excitations, polarized double zeta basis set, with zero point energy corrections) lead to a highly Jahn–Teller distorted GeH$_4^+$ ground state, with $C_2$ symmetry, approaching a GeH$_4^+$·H$_2$ complex. In fact, the dissociation energy to GeH$_2^+$ + H$_2$ is found to be only 4.9 kcal/mol, while the process forming GeH$_3^+$ + H is computed to require 25.5 kcal/mol. These results are rather similar to the observations on SiH$_n^+$, both theoretical$^{16,19}$ and experimental.$^1$ Their calculated adiabatic ionization potential of GeH$_4$ (10.2 eV) is far below the value (11.3 eV) obtained from photoelectron spectroscopy.$^{21}$

Our goal in the experimental work to be presented below was to determine the successive bond energies as hydrogen atoms are removed from GeH$_4$, by a combination of appearance potentials of fragment ions and adiabatic ionization potentials of the GeH$_n$ ($n=1$–3) free radicals. The method used to determine these quantities is photoionization mass spectrometry. Chemical reaction is used to generate the free radicals in situ. A further goal was to examine the onset energy of GeH$_n^+$ (GeH$_n$).

II. EXPERIMENTAL ARRANGEMENT

The basic photoionization mass spectrometric apparatus has been described previously.$^{22}$ A tight (more enclosed) ionization chamber was used for studies of stable GeH$_4$, while a more open chamber was employed for the free radical experiments. The chemical reaction used for generating the GeH$_n$ radicals was hydrogen abstraction by fluorine atom interaction with GeH$_4$, analogous to an earlier study$^1$ of the products of the $F + \text{SiH}_4$ reaction. Additional experiments were performed using atomic hydrogen and atomic chlorine as reactants in an attempt to increase the yield of GeH$_2$, but these experiments were less successful.

III. EXPERIMENTAL RESULTS

Mass spectrometric studies with germanium compounds are more difficult than, e.g., silicon compounds, be-
cause of the wide distribution of isotopes. The isotopic abundances recommended by IUPAC (International Union of Pure and Applied Chemistry) are M70 (20.5\%), M72 (27.4\%), M73 (7.8\%), M74 (36.5\%), and M76 (7.8\%). This property causes overlap problems with different GeH\textsuperscript{+} species and also reduces the effective abundance of any desired species. Hence, one must devise the most effective strategy for studying each particular species.

A. Photoionization of GeH\textsubscript{4}

It is illustrative to compare the photoionization mass spectrum of GeH\textsubscript{4} with the He I photoelectron spectrum. In Fig. 1(a), the He I photoelectron spectrum of the first two (valence) bands\textsuperscript{21} is reproduced. An overview of the photoionization mass spectrum (plotted on a photon energy scale, to conform to the photoelectron scale) is given in Fig. 1(b). In constructing this figure, GeH\textsubscript{4} was measured at the m/e = 80 position at shorter wavelengths, where contamination from other species was possible at other masses. To longer wavelengths, m/e = 78 and m/e = 76 were used. This strategy, while avoiding isotopic contamination, had the disadvantage that, when m/e = 80 was monitored, the inherently weak GeH\textsubscript{4} could be measured by more than an order of magnitude, since \(^{76}\text{Ge}\) has a small isotopic abundance. The GeH\textsuperscript{+} was monitored at m/e = 77, which is essentially isotopically pure and fairly abundant, until the threshold of GeH\textsuperscript{+} (GeH\textsubscript{4}). The GeH\textsuperscript{+} species was measured at m/e = 72. The spectrum shown in Fig. 1(b) has been corrected for the various isotopic abundances and represents the fragmentation pattern of GeH\textsubscript{4}. Comparison of Figs. 1(a) and 1(b) reveals that a weak but significant GeH\textsuperscript{+} intensity in Fig. 1(b) extends well below (\(\sim 0.8\) eV below) the adiabatic threshold (11.3 eV) observed in the photoelectron spectrum (PES) [Fig. 1(a)]. Even the first fragment ion GeH\textsuperscript{+} has its onset below 11.3 eV, but begins to increase significantly at approximately the adiabatic threshold observed in PES. The second fragment GeH\textsuperscript{+} approaches the background level very gradually, even though its apparent onset occurs within the Franck-Condon region represented by Fig. 1(a).

1. GeH\textsuperscript{+} (GeH\textsubscript{4})

The photoion yield curve of GeH\textsubscript{4} from GeH\textsubscript{4} is shown in greater detail in Fig. 2. Some rounded step structure is apparent as the curve approaches the threshold. There is some tailing very near to threshold, which may be due to a hot band, or to a very weak Franck-Condon factor. We choose the adiabatic threshold at 1178 Å = 10.53 eV, but it may be as low as 1188 Å = 10.44 eV. As mentioned earlier, this is \(\sim 0.8\) eV below the adiabatic threshold observed in PES\textsuperscript{21} (nine or ten vibrational quanta), but \(\sim 0.3\) eV higher than the value obtained by Kudo and Nagase.\textsuperscript{18}

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (a) He I photoelectron spectrum of the first band of GeH\textsubscript{4} (from Ref. 21). (b) Photoion yield of the various GeH\textsuperscript{+} species from GeH\textsubscript{4} as a function of photon energy. This spectrum has been corrected for isotopic abundance. O—GeH\textsuperscript{+}; □—GeH\textsubscript{2}; Δ—GeH\textsubscript{2}; ◊—GeH\textsuperscript{+}; ▽—Ge\textsuperscript{+}. J. Chem. Phys., Vol. 92, No. 3, 1 February 1990
FIG. 2. The photoion yield curve of GeH$_4^+$ (GeH$_4$).

The steplike features in the GeH$_4^+$ have about the same spacing as the vibrational features in the photoelectron spectrum, which are observed at higher energy. The steplike features cease and the curve begins to decline below \( \sim 1160 \text{Å} \), just where the first fragment (GeH$_2^+$) begins to appear. In the region below 1160 Å, a new type of structure appears, perhaps due to autoionization or selective predissociation. Not only is GeH$_4^+$ very weak, but it has only been observed in a relatively narrow wavelength region, between \( \sim 1080-1180 \text{Å} \). This general behavior (weak parent ion, step structure, narrow window of observation) is very similar to that displayed by SiH$_4^+$ (SiH$_4$).\(^1\) Both GeH$_4^+$ and SiH$_4^+$ would be very difficult to detect by electron impact mass spectrometry.

2. GeH$_2^+$ (GeH$_4$)

This is the first fragment ion. A detailed photoion yield curve of GeH$_2^+$ (GeH$_4$) in the threshold region is displayed.

FIG. 3. The photoion yield curve of GeH$_2^+$ (GeH$_4$) near threshold.
in Fig. 3. Although its onset is below the adiabatic threshold observed in PES and hence it occurs in a weak Franck–Condon region, the approach to threshold is not far from linear. The extrapolated appearance potential is $1156 \pm 1 \text{Å} = 10.72 \pm 0.009 \text{eV}$. When corrected for internal thermal energy of $\text{GeH}_4$ (1.097 kcal/mol at 300 K), the 0 K threshold becomes $10.772 \pm 0.009 \text{eV}$.

This value, and the other appearance potentials (A.P.) from $\text{GeH}_4$ obtained in this work, are summarized in Table 1. Also listed in this table are the results of two studies$^{24,25}$ by electron impact mass spectrometry and two recent ab initio calculations.$^{18,27}$ As implied above, neither electron impact study detected $\text{GeH}_4^+$. More surprisingly, both electron impact measurements indicate that A.P.($\text{GeH}_4^+$) is 1.0 eV lower than A.P.($\text{GeH}_2^+$), whereas the present results (vide infra) and the $ab$ initio calculations conclude that A.P.($\text{GeH}_4^+$) < A.P.($\text{GeH}_2^+$), by 0.76–0.9 eV. Kudo and Nagase$^{18}$ have calculated 4.9 kcal/mol for the enthalpy of the reaction

$$\text{GeH}_4^+ \rightarrow \text{GeH}_2^+ + \text{H}_2$$

(1)

whereas Binning and Curtiss$^{27}$ obtained 7.5 kcal/mol. Both calculations were performed at a fairly high level of theory. If we utilize our adiabatic ionization potential of $\text{GeH}_4$ and our appearance potential of $\text{GeH}_4^+$, we obtain 5.6 ± 0.5 kcal/mol for the endothermicity of reaction (1), in rather good agreement with both calculations.

3. $\text{GeH}_4^+$ ($\text{GeH}_3$)

Initial attempts at determining the threshold for this process were plagued by an extended region of curvature near the onset, encompassing at least 50 Å [Fig. 4(a)]. Various possible causes were examined, including gradually increasing Franck–Condon factors, scattered light, and pressure effects. Since $\text{GeH}_2^+$ ($\text{GeH}_4$) simulates the Franck–Condon effects in this region, an experiment was performed in which the ratio of intensities ($\text{GeH}_3^+$)/($\text{GeH}_4^+$) was measured as a function of wavelength, with the anticipation that the gradually increasing ionization probability would be canceled in the ratio. This measurement [Fig. 4(b)] did, in fact, yield a much less curved function vs wavelength, but with a relatively high “background” ratio, more or less flat, at longer wavelengths. The experiment was repeated, with the $\text{GeH}_4$ pressure reduced by a factor of ~5. A similar curve was obtained [Fig. 4(c)]; however, the ($\text{GeH}_3^+$)/($\text{GeH}_4^+$) ratio was reduced in the quasilinear region by about 10% and the background ratio diminished by a factor of 3–4. These observations implied that bimolecular collisional effects were playing a role. Collisional decomposition of $\text{GeH}_4^+$ could not be implicated, since the abundance of parent ion was too low to account for the tail in the photoion yield of $\text{GeH}_3^+$. It seems most likely that the ion–molecule reaction

$$\text{GeH}_2^+ + \text{GeH}_4 \rightarrow \text{GeH}_3^+ + \text{GeH}_3$$

(2)

is responsible for this background. Northrop and Lampe$^{25}$ report that this reaction has a rate constant of $2.8 \times 10^{-10}$ cm$^3$ molecule s, i.e., it is very fast. We shall show below that this reaction is exothermic, by about 4 kcal/mol. An upper limit to the threshold for $\text{GeH}_3^+$ ($\text{GeH}_4$) extracted from Figs. 4(b) and 4(c) is $1068 \pm 1 \text{Å} = 11.60 \pm 0.01 \text{eV}$, or $11.65 \pm 0.01 \text{eV}$ at 0 K.

4. $\text{GeH}_3^+$ ($\text{GeH}_3$)

The process responsible for this ion is presumed to be

$$\text{GeH}_4 \rightarrow \text{GeH}_3^+ + \text{H}_2 + \text{H} + \epsilon.$$  (3)

It is weak and has a threshold < 12.9 eV [see Fig. 1(b)]. The interesting aspect of this process is the relatively intense, broad peak centered at 15.5 eV and the autoionizing structure on the high energy side of this broad peak. A similar behavior was observed with $\text{SiH}_4^+$ ($\text{SiH}_3$),$^1$ but in the $\text{GeH}_3^+$ case, the peaks are much broader than the instrumental resolution and they display an asymmetric shape. The separation between peaks (~ 1560 cm$^{-1}$) and the general pattern (four relatively prominent peaks, one weaker one) are rather similar to the photoelectron spectrum of the inner band ($a_1$)$^{-1}$ of $\text{GeH}_4$ (see Fig. 1 and Ref. 21). From the adiabatic ionization potential (IP) reported for this band (18.21 eV) and the energy of the first autoionization peak in the $\text{GeH}_3^+$ photoionization spectrum, we calculate an effective quantum number $n^* = 2.503$. The uppermost occupied $a_1$ orbital in $\text{GeH}_4$ is expected to be primarily a 4s-like germanium orbital.$^{21}$ Rydberg transitions emanating from this orbital can be anticipated to be $p$-like in their quantum defect ($\delta = n - n^*$). The observations bear this out. The predict-

### Table 1. Appearance potentials of $\text{GeH}_3^+$ species from $\text{GeH}_4$ (eV).

<table>
<thead>
<tr>
<th>Species</th>
<th>Present data (0 K)</th>
<th>Saalfeld and Svcek$^a$</th>
<th>Northrop and Lange$^b$</th>
<th>Kudo and Nagase$^c$</th>
<th>Binning and Curtiss$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{GeH}_4^+$</td>
<td>&lt;10.53 ± 0.02</td>
<td>...</td>
<td>...</td>
<td>10.2</td>
<td>10.47</td>
</tr>
<tr>
<td>$\text{GeH}_3^+$</td>
<td>&lt;11.65 ± 0.01</td>
<td>10.8 ± 0.3</td>
<td>10.9 ± 0.2</td>
<td>11.3</td>
<td>11.60</td>
</tr>
<tr>
<td>$\text{GeH}_4^+$</td>
<td>10.77 ± 0.009</td>
<td>11.8 ± 0.2</td>
<td>11.9 ± 0.2</td>
<td>10.4</td>
<td>10.79</td>
</tr>
<tr>
<td>$\text{GeH}_3^+$</td>
<td>&lt;12.9</td>
<td>11.3 ± 0.3</td>
<td>11.2 ± 0.2</td>
<td>...</td>
<td>12.41</td>
</tr>
<tr>
<td>$\text{Ge}^+$</td>
<td>&lt;11.48</td>
<td>10.7 ± 0.2</td>
<td>10.4 ± 0.2</td>
<td>...</td>
<td>10.94</td>
</tr>
</tbody>
</table>

$^a$ Reference 24.  
$^b$ Reference 25.  
$^c$ Reference 18.  
$^d$ Reference 27.
5. Ge⁺ (GeH₄)

The most likely origin of Ge⁺ is the process

\[ \text{GeH}_4 \rightarrow \text{Ge}^+ + 2\text{H}_2 + e^- \]  \hspace{1cm} (4)

It has a lower threshold than GeH⁺, < 11.48 eV, and is more intense [see Fig. 1(b)]. There is less evidence for structure in this curve than in GeH⁺. There are broad features, which are similar to those in GeH⁺ and Ge⁺, at ~13.5 and ~15.5 eV.

Due to the nature of these processes, the threshold of both Ge⁺ and GeH⁺ are regarded as upper limits and are not useful for thermochemical determinations.

B. Photoionization of the free radicals

1. GeH₂⁺ (GeH₂)

The photoion yield curve of GeH₂⁺ (GeH₂) is displayed in Fig. 5. Only the peaks in the hydrogen light source spectrum were employed in these measurements. Step structure is readily apparent in the region near threshold, with an average spacing of 8.83 Å = 393 ± 15 cm⁻¹. This is most probably the out-of-plane bending frequency excited in the transition from pyramidal GeH₂ to planar or near planar GeH₂⁺. The adiabatic ionization potential is at least as low as 1560 ± 1 Å = 7.94 ± 0.005 eV. There is a still weaker feature at 1568 ± 1 Å ≈ 7.90 ± 0.005 eV, but this may be a hot band. The GeH₂⁺ photoion yield curve approaches a plateau at ~1380 Å and then increases rather sharply to ~1200 Å, beyond which it begins to decline. The more rapid increase in ion yield below ~1380 Å is suggestive of the onset of an excited state of GeH₂⁺.

2. GeH⁺ (GeH₂)

The GeH⁺ fragment ion from photodissociative ionization of GeH₂ was measured at \( m/e = 71 \) as a function of wavelength and is shown in Fig. 6. The region near the onset (1380 ± 5 Å = 8.98 ± 0.03 eV) is extremely weak. A much sharper increase occurs below ~1285 Å. Assuming that the GeH₂ species has an internal energy corresponding to 300 K, we compute a 0 K threshold for GeH⁺ (GeH₂) to occur at ~9.92 eV.

The sharp increase at \( \lambda < 1285 \) Å is again suggestive of an excited state of GeH⁺ which readily decomposes into GeH⁺ + H₂. A similar behavior (weak signal near threshold, more abrupt increase at higher energy) was observed in the corresponding photodissociative ionization process involving SiH₃⁺. No experimental data have yet been published on the first excited state of GeH⁺ and SiH₃⁺. Available calculations indicate that the formation of such an excited state should occur by single electron ejection from an \( e^- \) type orbital, which allows for Jahn–Teller distortion. One may speculate that the more rapid increase in GeH⁺ (GeH₂), and the corresponding increase in SiH⁺ (SiH₃), occurs when a Jahn–Teller state is accessed which has a larger ionization and/or dissociative ionization probability.
3. GeH₂⁺ (GeH₂)

In the related study of the SiH₂ produced by the successive abstraction reactions with atomic fluorine, little difficulty was encountered in observing SiH₂⁺ (SiH₂). In fact, evidence was presented for the formation and detection of both the \( X^1A_1 \) and \( a^3B_1 \) states of SiH₂. Since the Ge–H bonds are expected to be weaker than the Si–H bonds, it was anticipated that the detection of GeH₂⁺ (GeH₂) would be straightforward. Instead, a weak signal was observed at \( m/e = 72 \), most of which was \(^{72}\text{Ge}^+\), rather than \(^{70}\text{Ge}^+\), as judged by a corresponding signal at \( m/e = 70 \) (\(^{70}\text{Ge}^+\)). The \( m/e = 70 \) signal was followed to longer wavelengths and was consistent with the presence of atomic germanium in the reaction vessel. In the corresponding SiH₄ reaction, \(^1\text{SiH}^+\) (SiH) could be detected, but not atomic silicon. We speculate that GeH₂ is generated in the F + GeH₄ reaction, but that most of it is decomposed upon collision with other molecules or on the wall, producing atomic germanium. A few such collisions are expected in our reaction cell before the species can exit through the 5 mm orifice. If GeH₂ is formed in both \( X^1A_1 \) and \( a^3B_1 \) states, and the branching ratio favors \( a^3B_1 \), this excited species may more readily decompose into Ge + H₂. A further indication of the rapid loss of GeH₂ is the absence of any detectable signal for GeH⁺ (GeH). Presumably, GeH would be formed by the
F + GeH₃ reaction; the weakness of the GeH₃ signal makes the probability of formation of GeH less likely.

Despite these difficulties, an upper limit to the adiabatic ionization potential of GeH₃ was obtained by laborious measurement of the signal at m/e = 72 as a function of wavelength. The ionization potential of atomic germanium is 7.8995 eV ≈ 1569.5 Å. That of GeH₃ is expected to be considerably higher. One observes (Fig. 7) a somewhat higher value for this signal between 1200–1300 Å and then a rather rapid decline to ~ 1340 Å. The background to longer wavelength is attributable to ⁷²Ge⁺. Hence, the adiabatic ionization potential of GeH₃ is < 9.25 eV ≈ 1340 Å. A much better measurement could undoubtedly be performed with monoisotopic Ge, since the signal would be five times stronger and the background of atomic germanium would be absent.

The adiabatic ionization potentials of the GeH₄ free radicals obtained in the current study are summarized in Table II. Also shown are the results of the recent ab initio calculations of Binning and Curtiss.²⁷

IV. INTERPRETATION OF RESULTS

A. Thermochemistry

Gunn and Green²⁹ measured the heat of formation of GeH₄ at 298 K and obtained + 21.6 ± 0.5 kcal/mol. This value (for some reason, 21.7 kcal/mol was used) has been erroneously converted to 0 K in various compilations,³⁰,³¹ but a more nearly correct value 24.29 kcal/mol is given in the National Bureau of Standards tabulation.³² The heat of formation of atomic germanium³ (0 K) is 88.2 ± 0.7 kcal/mol and that of atomic hydrogen² is 51.634 kcal/mol. By combining these quantities in appropriate stoichiometric fashion, one obtains 270.5 ± 0.9 kcal/mol for the heat of atomization of GeH₄.

From the present measurements, an upper limit to the appearance potential of GeH₄⁺ (GeH₄) is 11.65 ± 0.01 eV and the adiabatic ionization potential of GeH₃ is 7.948 eV. This leads to D₀(H₂Ge–H) < 3.70 kcal/mol. This value is almost certainly too high. The appearance potential of GeH₃⁺ (GeH₄) is very likely shifted to higher energy, since GeH₄⁺ is the second (higher energy) fragment. On the other hand, the value favored by Setser and co-workers,⁴ 78.0 ± 1.0 kcal/mol, may well be a lower limit, although they regard it as an upper limit. These authors have reacted F, Cl, and O with GeH₄. The reaction of choice⁴(a) involved F atoms and the exothermicity of this reaction was determined by the maximum excitation of HF product. This was corrected for thermal energy (3RT = 1.8 kcal/mol) and an activation energy of 0.5 kcal/mol. However, in an earlier paper,⁴(b) in which the F + GeH₄ reaction was described, they note that if they “... ignore the contribution of thermal energy to the reaction D(H–Ge₃) < 78.4 kcal/mol...” Clearly, the higher the excitation observed in product HF, the weaker is the H₂Ge–H bond energy. However, if some of the HF excitation derives from the initial internal energy of GeH₄, a corrected value taking into account this internal energy would increase the derived value of D₀(H₂Ge–H). The contribution of rotational energy may be most suspect. The B constant (inverse moment of inertia) of the spherical top GeH₃ molecule is 2.69 cm⁻¹, very nearly that (2.65 cm⁻¹) of the CD₄ molecule. The thermal distribution of rotational levels for a spherical top

\[ N_J \sim (2J + 1)^2e^{-B(J(J+1)/K)} \]

is given by Herzberg³³ for CD₄ at 300 K. One can see that, although the most probable value of J is about 10 (E₁₀ = 0.85 kcal/mol), a substantial fraction of the molecules have J > 15 (E₁₅ = 1.85 kcal/mol), and a not insignificant fraction have J > 20 (E₂₀ = 3.24 kcal/mol). Hence, a possible interpretation of the chemiluminescence experi-

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**FIG. 7.** The photoion yield curve of the m/e = 72 ion, generated in the F + GeH₄ reaction. This mass corresponds to ⁷⁰Ge⁺ and ⁷⁰GeH₃⁺. The decline to ~ 1335 Å corresponds to the onset region for ⁷⁰GeH₃⁺, the background to ⁷²Ge⁺.
 TABLE II. Ionization thresholds from GeH₄ free radicals (eV).  

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Present work</th>
<th>Calculation¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeH₄ → GeH⁺ + e</td>
<td>&lt;7.94 ± 0.005</td>
<td>7.92</td>
</tr>
<tr>
<td>GeH₄ → Ge⁺ + H₂ + e</td>
<td>&lt;9.02 ± 0.03</td>
<td>8.73</td>
</tr>
<tr>
<td>GeH₄ → Ge⁺ + e</td>
<td>&lt;9.25</td>
<td>9.09</td>
</tr>
<tr>
<td>GeH₄ → Ge⁺ + e</td>
<td>...</td>
<td>7.67 (7.74b)</td>
</tr>
</tbody>
</table>

¹Reference 27.
²With spin–orbit correction.

ments would lead to \( D_0 (\text{H}_5\text{Ge–H}) \approx 81 \text{ kcal/mol} \). We estimate that the kinetic shift in the appearance potential of GeH⁺⁺ (GeH₄) could be 3–4 kcal/mol, which would reduce \( D_0 (\text{H}_5\text{Ge–H}) \) from our upper limit of 85.5 to \( \approx 82 \text{ kcal/mol} \). Such a value would be in satisfactory agreement with the ionization results of Walsh and co-workers⁵ 83 ± 2.4 kcal/mol. On this basis, our current best estimate is 82 ± 2 kcal/mol for \( D_0 (\text{H}_5\text{Ge–H}) \). This implies \( \Delta H^s_{r0} (\text{GeH}_2) = 54.7 \pm 2 \text{ kcal/mol} \).

The appearance potential of GeH⁺⁺ (GeH₄) reported in this study, 10.777 ± 0.009 eV, should be a fairly reliable quantity. The GeH⁺⁺ is the first fragment and the approach to threshold is not far from linear. However, the difficulties encountered in the measurement of GeH⁺⁺ (GeH₂) enable us to extract only an upper limit \( <9.25 \text{ eV} \) for this adiabatic ionization potential. From this information, we can deduce \( \Delta H^0_{r0} \approx 1.522 \text{ eV} = 35.1 \text{ kcal/mol} \) for the decomposition reaction

\[
\text{GeH}_4 \rightarrow \text{GeH}_2 + \text{H}_2. \quad (6)
\]

Binning and Curtiss²⁷ have calculated 9.08 eV for the adiabatic ionization potential of GeH₂. With this value, the endothermicity of reaction (4) becomes 39.0 kcal/mol. This result is intriguingly close to the enthalpy inferred for thermal decomposition of germane to GeH₂ + H₂. Newman et al.³⁴ have performed shock tube studies and used Rice–Ramsberger–Kassel–Marcus (RRKM) theory to determine the activation energy for the forward (54.3 kcal/mol) and backward (15 ± 10 kcal/mol) reactions. The net decomposition energy is thus 39.3 ± 10 kcal/mol. Reference 5(b) cites unpublished work by Walsh which is equivalent to 35.3 ± 3 kcal/mol for this reaction. Devyatikh and Frolov,⁵⁵ have obtained 37.5 kcal/mol for the activation energy of the heterogeneous decomposition of GeH₄ on a germanium film surface, which apparently acts as a catalyst for this reaction. While the mechanism of this latter decomposition is not clear, it may be that the rate determining step is the decomposition to GeH₂ + H₂. The GeH₂ product should readily decompose to Ge (solid) + H₂.

From the endothermicity of reaction (6), we conclude that \( \Delta H^0_{r0} \approx 138.4 \text{ kcal/mol and, more probably, 141 ± 2} \text{ kcal/mol for the reaction}

\[
\text{GeH}_4 \rightarrow \text{GeH}_2 + 2\text{H}. \quad (7)
\]

With our choice of the H₅Ge–H bond energy, we infer \( D_0 (\text{H}_5\text{Ge–H}) > 56.4 \text{ kcal/mol and more probably 59 kcal/mol. Hence } \Delta H^s_{r0} (\text{GeH}_2) > 59.3 \text{ kcal/mol and, more probably, 61.8 kcal/mol.}

We are left with about 129.6 kcal/mol (\( <132.1 \text{ kcal/mol} \)) to apportion to the remaining bond energies. Since GeH was not detected in the present experiments, our conclusions are of necessity more speculative and dependent in part on other sources. We have measured the threshold for the reaction

\[
\text{GeH}_3 \rightarrow \text{GeH}^+ + \text{H}_2. \quad (8)
\]

to be \( <9.02 \text{ eV} \). Binning and Curtiss²⁷ have calculated the adiabatic ionization potential of GeH and obtained 7.66 eV. This seems a plausible value, based on the following considerations. The ionization potential of CH (10.64 eV)³ is 0.628 eV less than that of C (11.2676 eV).³⁶ The ionization potential of SiH (7.91 eV)¹ is 0.24 eV less than that of Si (8.1517 eV).³⁷ By extrapolating this trend, we anticipate that IP(GeH) will be less than that of GeH (7.8995 eV)²⁸ by an increment less than 0.24 eV. Also, we expect IP(GeH) to be less than IP(SiH). Accepting the value of Binning and Curtiss for IP(GeH), we can deduce \( \Delta H^0_{r0} \approx 31.4 \text{ kcal/mol for the reaction}

\[
\text{GeH}_3 \rightarrow \text{GeH} + \text{H}_2. \quad (9)
\]

With our previously selected value for \( \Delta H^s_{r0} (\text{GeH}_3) \), this enthalpy leads to \( \Delta H^s_{r0} (\text{GeH}) \approx 86 \text{ kcal/mol, or } D_0 (\text{GeH}) > 2.33 \text{ eV.}

Thus, 2.33 eV \( < D_0 (\text{GeH}) < 3.3 \text{ eV, the latter value being the upper limit established by a predissociation. The calculated and recommended value of Balasubramanian and Li,³⁰ 2.74 ± 0.05 eV, meets this criterion. At this time, it is the most reliable value for } D_0 (\text{GeH}).

With this choice, \( D_0 (\text{HGe–H}) < 68.9 \text{ kcal/mol and, more probably, 66.4} \text{ kcal/mol. The heats of formation of the GeHₙ and GeH⁺ₙ species deduced from the above analysis are summarized in Table III. The stepwise bond energies of GeHₙ₋₁–H (n = 1–4) are listed in Table IV.}

With the current data on GeHₙ bond energies, the recently established SiHₙ,¹ and previously known CHₙ,³ it is useful to draw some comparisons. In order to normalize these observations, we divide each bond energy by the average bond energy for that system, i.e., 98.1, 75.7, and 67.7 kcal/mol for CHₙ, SiHₙ, and GeH₄, respectively. A plot of this fractional bond energy vs the type of bond (M–H, H–M–H, etc.) appears in Fig. 8. It is immediately apparent that the pattern of GeHₙ bonding is quite similar to that of SiHₙ, but markedly different from CHₙ. The H₅–H bond is the weakest one in GeHₙ and SiHₙ, but the strongest in CHₙ. Goddard and Harding have prejudged this qualitative behavior in their review article.³⁸ In particular, the decrease in
TABLE III. Heats of formation of GeH₄ and GeH₄⁺.

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Setser and co-workers</th>
<th>Walsh and co-workers</th>
<th>Binning and Curtiss</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH₃</td>
<td>&lt;58.1</td>
<td>50.6</td>
<td>55.2 ± 2.4</td>
<td>50.0 [52.8]</td>
</tr>
<tr>
<td></td>
<td>(54.7 ± 2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH₂</td>
<td>&gt;59.3</td>
<td>...</td>
<td>60.4 ± 3.8</td>
<td>56.4 [59.2]</td>
</tr>
<tr>
<td></td>
<td>(61.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GeH⁺</td>
<td>&lt;86</td>
<td>...</td>
<td>...</td>
<td>74.9 [76.0]</td>
</tr>
<tr>
<td></td>
<td>(76.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ΔHᵣₒ (GeH₄⁺) (kcal/mol)

GeH₄⁺ 267         258 [261]
GeH₃⁺ 241         232.6 [235.4]
GeH₂⁺ <272.6 ± 0.2 266.0 [268.8]
GeH⁺ <266         251.7 [254.5]

*a* Quantities in parentheses are more probable values.

*b* Reference 4.

*c* Reference 5.

*d* Reference 27. Quantities in square brackets include an estimated spin–orbit correction.

*e* Based on ΔHᵣₒ = 21.6 ± 0.5 kcal/mol from Ref. 28, corrected to 0 K.

The bonding strength between HM–H and H₂M–H for SiH₄ and GeH₄ is attributed to the need for unpairing the spins (noting that both SiH₄ and GeH₂ have ¹A₁ ground states), whereas this is not necessary for CH₂ (which has a ²B₁ ground state).

The strikingly similar pattern of SiH₄ and GeH₄ suggests that the big change occurs between first row and second row elements and that SnH₄ bond strengths may be predicted by knowing the atomization energy and making use of Fig. 8. Thus, from ΔHᵣ (SnH₄) = 41.8 ± 0.5 kcal/mol²⁹,³² and ΔHᵣ (Sn₉g) = 72.0 ± 0.2 kcal/mol,³³ the atomization energy is 236.7 ± 0.5 kcal/mol, or an average bond energy of 59.2 kcal/mol. Using Fig. 8, we estimate (kcal/mol) D₀(Sn–H) = 55, D₀(HSn–H) = 58, D₀(H₂Sn–H) = 51.5, and D₀(H₃Sn–H) = 71.6. The only experimental value available for comparison is D₀(Sn–H) < 62.9 kcal/mol based on an observed predissociation. However, a rather extensive relativistic quantum mechanical calculation³⁴ yields D₀(Sn–H) = 53 kcal/mol.

B. Implications from the thermochemical results

1. The ion–molecule reaction

The data contained in Table III allow us to evaluate the enthalpy of the ion–molecule reaction (2). The rigorous upper limit for ΔHᵣₒ (GeH₄) and ΔHᵣₒ (GeH₄⁺) leads to ΔHᵣₒ < -2.3 kcal/mol, while the more probable values for these quantities yield ΔHᵣₒ = -4.1 kcal/mol. The evidence in our data for a background which is quadratic in pressure is consistent with reaction (2) being slightly exoergic and having no significant activation barrier. From data given in Ref. 1, the analogous reaction of SiH₄⁺ with SiH₄ is exoergic by about 3 kcal/mol. This latter reaction has been measured³⁵ to have a rate constant > 10⁻²⁵ cm³/molecule s, i.e., typical of

TABLE IV. Stepwise bond energies (kcal/mol, 0 K).

<table>
<thead>
<tr>
<th></th>
<th>Present study</th>
<th>Setser and co-workers</th>
<th>Walsh and co-workers</th>
<th>Klynning and Lindgren</th>
<th>Calculations</th>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃Ge–H</td>
<td>&lt; 85.5 (82 ± 2)</td>
<td>78.0 ± 1.0</td>
<td>82.7 ± 2.4</td>
<td>...</td>
<td>84.8°</td>
</tr>
<tr>
<td>H₂Ge–H</td>
<td>&gt; 56.4 (59)</td>
<td>...</td>
<td>56.9 ± 2.9</td>
<td>...</td>
<td>58.0°</td>
</tr>
<tr>
<td>H–Ge–H</td>
<td>&lt; 68.9 (66)</td>
<td>...</td>
<td>...</td>
<td>70.2° [68.5]</td>
<td></td>
</tr>
<tr>
<td>Ge–H</td>
<td>&gt; 53.7 (63)</td>
<td>...</td>
<td>...</td>
<td>&lt; 76.1</td>
<td>63.2 ± 1°, 64.9° [63.8]</td>
</tr>
</tbody>
</table>

*a* Quantities in parentheses are more probable values.

*b* Reference 4.

*c* Reference 5.

*d* Reference 9.

*e* Reference 27. Quantities in square brackets include an estimated spin–orbit correction.

*f* Reference 10.
an exoergic, very rapid ion–molecule reaction, which appears also to be the case for the GeH$_4^+$ + GeH$_4$ reaction.$^{25}$

2. The presence of atomic germanium

In our earlier studies$^1$ on the reaction products from the F + SiH$_4$ reaction, we observed SiH$_5$, SiH$_2$ (both $X'A_1$ and $a'3B_1$) and SiH, but no Si(g). In the present studies of the F + GeH$_4$ reaction, we observe GeH$_3$, some GeH$_2$, no GeH, but some Ge(g). Our interpretation of this difference in behavior is based on the relative stability of SiH$_2$ and GeH$_2$.

It is now fairly well established$^1$ that $\Delta H_{f0}^{\circ}$ (SiH$_2$) = 65.6 ± 2 kcal/mol. The heat of formation of atomic silicon$^3$ is 106.5 ± 2 kcal/mol. Hence, we compute

$$\text{SiH}_2(X'A_1) \rightarrow \text{Si}(g) + \text{H}_2, \quad \Delta H_{f0}^{\circ} = 40.9 \text{kcal/mol}.$$ (10)

The $a'3B_1$ state of SiH$_2$, which lies 21.0 ± 0.7 kcal/mol$^1$ above $X'A_1$, is still stable with respect to these decomposition products by 19.9 ± 2.8 kcal/mol. In the present work, we have established that $\Delta H_{f0}^{\circ}$ (GeH$_2$) > 59.35 kcal/mol and, more probably, 61.8 kcal/mol. The heat of formation$^3$ of atomic germanium is 88.2 ± 0.7 kcal/mol. From this information, we compute

$$\text{GeH}_2 \rightarrow \text{Ge}(g) + \text{H}_2, \quad \Delta H_{f0}^{\circ} < 28.9 \text{kcal/mol}$$ (11) and, more probably, $\Delta H_{f0}^{\circ} = 26.4 \text{kcal/mol}$. Several calculations$^{11-14}$ cited in the Introduction conclude that the ground state of GeH$_2$ is $^1A_1$ (as in SiH$_2$) and the $a'3B_1$ state lies 23 ± 2 kcal/mol above $^1A_1$. Hence, the current best estimate is that GeH$_2(a'3B_1)$ is barely stable with respect to Ge(g) + H$_2$. There is sufficient uncertainty in the ionization potential of GeH$_2$ and the singlet–triplet separation to allow for GeH$_2(a'3B_1)$ to be unstable. If this is the case, and if the accommodation coefficient of atomic germanium on the surface of our reaction chamber is significantly less than unity, then atomic germanium could survive and be detected in our experiment. This would appear to be a plausible explanation for the stated observations. It suggests that the reaction F + GeH$_3$ generates GeH$_2(a'3B_1)$ in at least comparable abundance to $X'A_1$.

C. Structural implications

1. GeH$_4^+$

The weak intensity of GeH$_4^+$, and the very large (0.8 eV) difference between our observed adiabatic ionization potential and that deduced from photoelectron spectroscopy strongly support the conclusion of Kudo and Nagase,$^{18}$ i.e., GeH$_4^+$ in its ground state must have a structure very far from tetrahedral. Their conclusion that this GeH$_4^+$ structure looks like GeH$_2^+$ + H$_2$, with $C_s$ symmetry, is very similar to the earlier results$^{19,20}$ on SiH$_4^+$.

2. GeH$_3^+$

Neutral GeH$_3$ appears to be less pyramidal$^{41}$ (i.e., closer to planar) than SiH$_3$. Since the ground state of SiH$_3^+$ has been calculated to be planar, it is quite likely that the ground state of GeH$_3^+$ is also planar. The next deeper lying occupied orbital in both SiH$_3$ and GeH$_3$ has $e$ symmetry. Single electron ejection from this orbital should produce the first excited state of the cation, which should be subject to Jahn–Teller distortion. The unusual behavior of the photoion yield curves in both SiH$_3^+$ (SiH$_3$) and GeH$_3^+$ (GeH$_3$), displaying a very gradual increase from threshold, and then (at higher energy) a more abrupt increase are believed to reflect the Franck–Condor probabilities in the excitation of pyramidal GeH$_3$ (SiH$_3$) to the Jahn–Teller distorted states.

V. CONCLUSIONS

The adiabatic ionization potential of GeH$_4$ has been measured to be <10.53 eV (perhaps as low as 10.44 eV) much lower than the value (11.3 eV) obtained by photoelectron spectroscopy. The very weak GeH$_4^+$ signal between 10.5–11.3 eV implies a large Jahn–Teller distortion of GeH$_4^+$ from a tetrahedral structure. The appearance potential of GeH$_4^+$ (GeH$_4$) is <10.77 ± 0.009 eV; that of GeH$_3^+$ (GeH$_3$) is <11.65 ± 0.01 eV. The free radicals GeH$_3$ and GeH$_2$ have been generated by the F + GeH$_4$ reaction. The adiabatic ionization potential of GeH$_3$ is 7.94 ± 0.005 eV; that of GeH$_2$ is <9.25 eV. The appearance potential of GeH$_2^+$ (GeH$_2$) is <9.02 eV. These data, together with auxiliary information, lead to the following heats of formation in kcal/mol at 0 K (more probable values in parentheses):

$$\text{GeH}_3 < 58.1 (54.7 \pm 2) ; \quad \text{GeH}_2 > 59.3 (61.8) ;$$
$$\text{GeH} < 86 (76.8).$$

Corresponding values for the cations are

$$\text{GeH}_4^+ = 267 ; \quad \text{GeH}_3^+ > 241 (238.5) ;$$
$$\text{GeH}_2^+ > 272.6 \pm 0.2 ; \quad \text{GeH}^+ < 266.$$
F + GeH₄ reaction is interpreted to result from the instability of GeH₂ (a \( \alpha^3B_1 \)) to decomposition into Ge(g) + H₂.

An autoionization band is observed in the GeH⁺ (GeH₄) photoion yield curve (and also, less markedly, in GeH₂ and GeH₃⁺) which is assigned to an \( \alpha_1 \rightarrow 5p \) transition in GeH₄.

ACKNOWLEDGMENT

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