Spectroscopic Constants and Potential Energy Curves of GeH⁺

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Theoretical calculations of spectroscopic constants and potential energy curves of 13 electronic states of GeH⁺ are obtained. We employed complete active space MCSCF followed by CI calculations to obtain the spectroscopic constants of GeH⁺. The theoretical IP of the Ge atom (7.68 eV) was found to be in good agreement with an experimental value of 7.88 eV. The ground state of GeH⁺ was found to be a 1Σ⁺ state with rₑ = 1.576 Å, ωₑ = 2024 cm⁻¹, and Dₑ = 2.95 eV in excellent agreement with the known experimental results. The GeH⁺ ion was found to have a larger Dₑ than the neutral GeH molecule (Dₑ = 2.81 eV). Our calculations confirm the experimentally observed a³Π-X¹Σ⁺ transition and predict other transitions which are yet to be observed.

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INTRODUCTION

Spectroscopic constants of group (IV) hydrides and ions such as SiHₙ, SiHₙ⁺, GeHₙ, and GeHₙ⁺ are of interest (1–7) since they are source materials for group (IV) semiconductor elements in chemical vapor deposition (8–15). Dissociation energies of the fourth-row hydrides have been the topics of several studies (8–15). Hence understanding the energetics and spectroscopic constants of such species could be useful in proposing plausible mechanisms for the processes involved in the chemical deposition of such elements.

Photoelectron spectroscopic and photoionization techniques are used to probe the electronic states of ionic species (8–10, 16, 17). Theoretical study of the electronic states of ions could thus be useful in our understanding of the photoelectron spectrum of such species. Tsuji et al. (22, 23) observed the a³Π₀⁺,₁ ← X¹Σ⁺ transition of GeH⁺ excited by collisions of He(2³S) and He⁺ with GeH₄ in the helium afterflow. Recently, Binning and Curtiss (24) have carried out MP4 calculations on the ground state of GeH⁺. The objective of this investigation is to obtain potential energy curves and spectroscopic constants of low-lying electronic states of GeH⁺.

METHOD OF CALCULATIONS

The electronic states of GeH⁺ were investigated using complete active space MCSCF (CASSCF) and first-order CI calculations. In addition second-order CI calculations were carried out on the ground state of GeH⁺. All computations employed relativistic effective core potentials for the Ge atom. The outer 3d¹⁰4s²4p² shells were explicitly retained in the calculations while the inner electrons were replaced by relativistic ECPs. The Gaussian RECPs generated by Hurley et al. (18) for the Ge atom are used.

¹ Camille and Henry Dreyfus Teacher–Scholar.
These authors have also optimized a 3s3p4d valence Gaussian basis set for the 3P ground state of the Ge atom. This was augmented by a set of diffuse s, p, and two sets of d-type polarization functions. The three large-exponent d functions were contracted. This resulted in a (4s4p6d/4s4p4d) basis set for the Ge atom. For the hydrogen atom we used van Duijneveldt’s (5s1p/3s1p) basis set.

The orbitals for higher-order CI calculations were generated using the CASSCF method, which is a MCSCF calculation in the full CI space generated by valence electrons distributed among the valence orbitals of the separated atoms. The 4s and 4p orbitals of Ge and H 1s orbitals constituted the active space. These orbitals correlated into three a1, one b2, and one b1 orbital in the C2v group. The four outer electrons of GeH+ were distributed in all possible ways among these five orbitals in the CASSCF method. The 3d10 shell of the Ge atom was allowed to relax at the CASSCF stage but no excitations from this shell were allowed at both the CASSCF and the FOCI stages. Separate calculations were made for various spatial and spin symmetries in the C2v group.

Following CASSCF calculations, first-order CI calculations were carried out. The FOCI calculations, in addition to all configurations in the CASSCF, included those configurations generated by distributing three electrons in the internal space and one electron in the external space in all possible ways. For the ground state and the first two excited 3Π and 1Π states, we also carried out SOCI calculations which included in addition to FOCI configurations all configurations generated by distributing two electrons in the internal space and two electrons in the external space in all possible ways. The CASSCF, FOCI, and SOCI calculations were carried out by Balasubramanian’s (19) modified version of ALCHEMY II codes2 to include relativistic ECPs.

RESULTS AND DISCUSSION

Table I shows the possible low-lying electronic states of GeH+ and their dissociation limits. The asymptotic energy separations of the electronic states of GeH+ were obtained from the CASSCF/FOCI method and the corresponding experimental atomic energy separations from Moore’s tables (20). As seen from Table I, the theoretical energy separations of Ge+ are in good agreement with the corresponding experimental values. For most of the electronic states of Ge+ the theoretical values are lower than the corresponding experimental values. The agreement of theoretical and experimental energies of the Rydberg (4s25s1)2S state of Ge+ in Table I is especially worth noting since the (3s3p4d) basis set is optimized for the valence orbitals. Similarly the theoretical ordering of valence and Rydberg states of Ge+ is in full accord with the corresponding experimental ordering.

The ionization potential of the germanium atom was also computed using the CASSCF/SOCI method as the energy separation of the ground state of GeH and GeH+ at R = 8.0 Å. The value obtained this way gives the energy required for

\[ \text{Ge}(3P) \rightarrow \text{Ge}^+(2P) + e^- \]

The theoretical SOCI value for the IP of Ge is calculated as 7.68 eV in very good agreement with an experimental value of 7.88 eV listed in Moore’s tables (20).

2 The major authors of ALCHEMY II are B. Liu, B. Lengsfield, and M. Yoshimine.
Table I shows the spectroscopic properties \((r_e, \omega_e, T_e,\) and \(D_e)\) of 13 electronic states of GeH\(^+\) lying within 98 000 cm\(^{-1}\) above the ground state. The ground state of GeH\(^+\) was found to be a closed-shell \(\Sigma^+\) state with \(r_e = 1.576\) Å, \(\omega_e = 2024\) cm\(^{-1}\), and \(D_e = 2.95\) eV. At the FOCl level the obtained spectroscopic constants are in reasonable agreement with the corresponding SOCl values. The \(\omega_e\) of the \(X^1\Sigma^+\) state determined by Tsuji et al. (23) from electronic emission spectra \((\omega_e = 2015\) cm\(^{-1}\)) is in excellent agreement with our calculated \(\omega_e = 2024\) cm\(^{-1}\).

The first excited state of GeH\(^+\) is a \(3\Pi\) state with \(r_e = 1.65\) Å and \(T_e = 18 930\) cm\(^{-1}\). The \(3\Pi_{0+}\) and \(3\Pi_1\) components of GeH\(^+\) should be observable since \(3\Pi_{0-} - 1\Sigma^+_0\) and \(3\Pi_1 - 1\Sigma^+_0\) transitions are allowed in an intermediate coupling. The transition moment for \(3\Pi_1 - 1\Sigma^+_0\) is expected to be nonnegligible through the \(3\Pi_1 - 1\Pi_1\) contamination.

Tsuji et al. (23) have observed the \(a^3\Pi_{0+} - X^1\Sigma^+\) and \(3\Pi_1 - X^1\Sigma^+\) transitions of GeH\(^+\). An additional weak band denoted \(z\) was also observed by these authors in the 510-nm region. The rotational analysis of the \(a^3\Pi_{0+,1} - X^1\Sigma^+\) system revealed the spectroscopic constants. The bandheads of the \(a^3\Pi_{0+} - X^1\Sigma^+\) and \(a^3\Pi_1 - X^1\Sigma^+\) systems were found to be at 18 611 and 19 146 cm\(^{-1}\), respectively. As seen from Table II, the theoretical SOCl \(T_e\) value of the \(3\Pi\) state is 18 930 cm\(^{-1}\). We expect the \(3\Pi_{0+} - 3\Pi_1\) spin–orbit energy separation to be at the most 1000 cm\(^{-1}\). Hence our calculated transition energy (18 930 cm\(^{-1}\)) for the \(3\Pi - 1\Sigma^+\) transition is in excellent agreement with the corresponding experimental value. The experimentally observed weak \(z\) band is most probably due to the \(3\Pi_{0-} - X^1\Sigma^+\) forbidden transition.

The \(1\Pi\) state was found to have only a shallow minimum at a long distance (see Fig. 1). The \(T_e\) value of the \(1\Pi\) state (23 270 cm\(^{-1}\)) at the SOCl level is quite comparable to the \(T_0\) value of the \(A^2\Pi-\chi\) system of GaH (22 745 cm\(^{-1}\)). Kronekvist et al. (21) have observed the \(A^2\Pi-\chi\) system of isoelectronic GaH. The \(A^2\Pi-\chi\) system of GaH was found
to be predissociated. The analogous system of GeH\(^+\) is probably observable only in absorption.

The spectroscopic constants of the \(^1\Pi\) state were found to be sensitive to the level of theoretical treatment since it has only a shallow minimum (Fig. 1). At a lower-order FOCI level of theory, the \(r_e\) of the \(^1\Pi\) state was much longer (3.16 Å). Consequently, further improvement of basis sets and the level of inclusion of electron correlation could bring in contraction of \(r_e\). We expect the \(r_e\) of the \(^1\Pi\) state to be between 2.1 and 2.7 Å. The large uncertainty is due to the shallow nature of the potential energy curve of this state.

As seen from Table II with the exception of the \(^3\Pi\) and \(^1\Pi\) excited states all other electronic states have \(T_e > 51,000\) cm\(^{-1}\). Thus there is a large density of states in the vacuum ultraviolet region.

The ground state parameters for the neutral GeH obtained at a comparable CASSCF/SOCI level of theory (2) are \(r_e = 1.59\) Å, \(\omega_e = 1921\) cm\(^{-1}\), and \(D_e = 2.81\) eV. This suggests that the photoelectron spectroscopic transition

\[
\text{GeH} (^2\Pi) \rightarrow \text{GeH}^+ (^1\Sigma^+) + e^-
\]

would involve \(\Delta r_e = -0.014\) Å and \(\Delta \omega_e = +103\) cm\(^{-1}\). The small shortening of the bond upon ionization is consistent with the fact that the removed electron composes from a nonbonding \(\pi\) orbital of the Ge atom. Thus the photoelectron spectrum cor-

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**TABLE II**

Spectroscopic Properties of GeH\(^+\)**

<table>
<thead>
<tr>
<th>State</th>
<th>(r_e (\text{Å}))</th>
<th>(\omega_e (\text{cm}^{-1}))</th>
<th>(T_e (\text{cm}^{-1}))</th>
<th>(D_e (\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\Sigma^+)</td>
<td>1.576</td>
<td>2024</td>
<td>0</td>
<td>2.95</td>
</tr>
<tr>
<td>(^3\Pi)</td>
<td>1.65</td>
<td>1343</td>
<td>18 930</td>
<td>0.60</td>
</tr>
<tr>
<td>(^1\Pi)</td>
<td>2.84</td>
<td>230</td>
<td>23 270</td>
<td></td>
</tr>
<tr>
<td>(^3\Sigma^-)</td>
<td>1.65</td>
<td>1121</td>
<td>51 891</td>
<td>2.24</td>
</tr>
<tr>
<td>(^3\Pi(II))</td>
<td>1.94</td>
<td>1366</td>
<td>58 936</td>
<td>1.37</td>
</tr>
<tr>
<td>(^1\Delta)</td>
<td>1.63</td>
<td>1669</td>
<td>66 439</td>
<td>2.24</td>
</tr>
<tr>
<td>(^1\Sigma^+ (II))</td>
<td>2.63</td>
<td>813</td>
<td>70 769</td>
<td>0.78</td>
</tr>
<tr>
<td>(^1\Sigma^+ (III))</td>
<td>3.43</td>
<td>983</td>
<td>75 616</td>
<td></td>
</tr>
<tr>
<td>(^1\Pi(II))</td>
<td>2.08</td>
<td>799</td>
<td>76 452</td>
<td></td>
</tr>
<tr>
<td>(^1\Sigma^+ (III))</td>
<td>1.71</td>
<td>1238</td>
<td>77 984</td>
<td></td>
</tr>
<tr>
<td>(^3\Sigma^+)</td>
<td>1.85</td>
<td>757</td>
<td>80 867</td>
<td></td>
</tr>
<tr>
<td>(^3\Delta)</td>
<td>2.32</td>
<td>616</td>
<td>83 994</td>
<td></td>
</tr>
<tr>
<td>(^1\Pi(III))</td>
<td>2.71</td>
<td>404</td>
<td>97 900</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Spectroscopic constants for the \(^1\Sigma^+\), \(^3\Pi\), and \(^1\Pi\) states were calculated using the SOCI method. All other spectroscopic constants were obtained using the FOCI method.
Corresponding to the smallest energy transition would have a relatively sharp peak. This is a consequence of the fact that the Franck-Condon factor for this transition would be large due to very small geometry changes. Hence there will be little vibration progression corresponding to the ground state transition.

The photoelectron transition GeH($X^2\Pi$) $\rightarrow$ GeH$^+$($^3\Pi$) + $e^-$ would however show considerable vibrational progression since $\Delta r_e$ for this transition is 0.1 Å. Hence the Franck-Condon factor for this transition would be smaller. This is due to the fact that the removed electron is a $2\sigma$ bonding electron in forming the $^3\Pi$ state. The next spectral peak corresponding to GeH($X^2\Pi$) $\rightarrow$ GeH$^+$($^1\Pi$) + $e^-$ is likely to be very diffuse and featureless since the $^1\Pi$ state is probably predissociated.

The adiabatic ionization potential of GeH was calculated as 7.47 eV, about 0.19 eV lower than the IP of the Ge atom (20). This is consistent with the larger $D_e$ of GeH$^+$ compared to GeH.

As seen from Fig. 1, the $^3\Pi$, $^1\Pi$, $^3\Sigma^+$, and $^1\Sigma^+$ curves dissociate into Ge$^+$(2$P$) + H(2$S$), consistent with the expected dissociation of these states shown in Table I.
The lowest $^{3}\Sigma^{+}$ state is repulsive. At longer distances the interaction between $^{1}\Pi_{1}, ^{3}\Pi_{1}$, and $^{3}\Sigma^{+}$ could become significant. The $^{1}\Sigma^{+}$(III) curve has double minima primarily due to valence–Rydberg avoided crossings.

Table III shows the leading configurations contributing to the electronic states of GeH$^{+}$. The ground state of GeH$^{+}$ is a mixture of $1\sigma^{2}2\sigma^{2}$ and $1\sigma^{2}1\pi^{2}$, although the former configuration dominates. The valence $^{3}\Pi$ and $^{1}\Pi$ states arise primarily from the $1\sigma^{2}2\sigma1\pi$ configuration. The $^{1}\Sigma^{+}$(II) and $^{1}\Sigma^{+}$(III) states are strong mixtures of valence and Rydberg configurations. This explains the double minima in the potential energy curve of the $^{1}\Sigma^{+}$(III) state (Fig. 1).

Next we compare the spectroscopic properties and potential energy curves of iso-electronic GaH. Kim and Balasubramanian (12) have carried out a comparable CASSCF/CI calculation on the low-lying electronic states of GaH. The ground state of GaH was found to be an $X^{1}\Sigma^{+}$ state with $r_c = 1.662$ Å and $\omega_c = 1612$ cm$^{-1}$. The smaller bond length and larger $\omega_c$ for GeH$^{+}$ are consistent with the strengthening of the $2\sigma$ orbital of GeH upon ionization. The $^{3}\Pi$ and $^{1}\Pi$ states of GaH were found to be 16 836 and 24 206 cm$^{-1}$ above the $X^{1}\Sigma^{+}$ ground state, respectively. As seen from Table II, this compares well with the corresponding values of 17 330 and 23 270 cm$^{-1}$ for GeH$^{+}$.

The potential energy curves of GeH$^{+}$ (Fig. 1) are quite akin to the corresponding curves of GaH [Fig. 1 in Ref. (12)]. The $^{1}\Sigma^{+}$(III) curve of GaH also exhibits double minima similar to the corresponding curves of GeH$^{+}$. However, there are differences in the electronic states of GeH$^{+}$ and GaH. The first excited state of the Ga atom is a

<table>
<thead>
<tr>
<th>State</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}\Sigma^{+}$</td>
<td>$1\sigma^{2}2\sigma^{2}$ (94), $1\sigma^{2}1\pi^{2}$ (4)</td>
</tr>
<tr>
<td>$^{3}\Pi$</td>
<td>$1\sigma^{2}2\sigma^{2}1\pi$ (94)</td>
</tr>
<tr>
<td>$^{1}\Pi$</td>
<td>$1\sigma^{2}2\sigma1\pi$ (95)</td>
</tr>
<tr>
<td>$^{3}\Sigma^-$</td>
<td>$1\sigma^{2}1\pi^{2}$ (86), $1\sigma2\sigma1\pi^{2}$ (8), $2\sigma^{2}1\pi^{2}$ (5)</td>
</tr>
<tr>
<td>$^{3}\Pi$(II)</td>
<td>$1\sigma^{2}2\pi^{2}$ (60), $1\sigma^{2}3\sigma1\pi$ (23), $1\sigma2\sigma3\sigma1\pi$ (8)</td>
</tr>
<tr>
<td>$^{1}\Delta$</td>
<td>$1\sigma^{2}1\pi^{2}$ (45), $1\sigma2\sigma1\pi^{2}$ (23), $1\sigma^{2}1\pi3\pi$ (4), $1\sigma^{2}1\pi3\pi$ (4), $1\sigma2\sigma3\pi$ (3), $1\sigma2\sigma3\pi$ (3)</td>
</tr>
<tr>
<td>$^{1}\Sigma^{+}$(II)</td>
<td>$1\sigma^{2}2\sigma3\sigma$ (47), $1\sigma^{2}3\sigma^{2}$ (10), $1\sigma^{2}\sigma\sigma_{Ry}$ (9), $1\sigma^{2}\sigma\sigma_{Ry}$ (8)</td>
</tr>
<tr>
<td>$^{1}\Sigma^{+}$(III)</td>
<td>$1\sigma^{2}2\sigma^{2}$ (33), $1\sigma^{2}2\sigma3\sigma$ (19), $1\sigma^{2}3\sigma^{2}$ (17), $1\sigma^{2}1\pi^{2}$ (8)</td>
</tr>
<tr>
<td>$^{1}\Pi$(II)</td>
<td>$1\sigma^{2}2\sigma1\pi$ (32), $1\sigma2\sigma3\sigma1\pi$ (19), $1\sigma3\sigma1\pi$ (16), $1\sigma^{2}3\sigma2\pi$ (9), $1\sigma^{2}3\sigma2\pi$ (9), $1\sigma^{2}\sigma\sigma_{Ry}$ (5)</td>
</tr>
<tr>
<td>$^{1}\Pi$$(III)$</td>
<td>$1\sigma^{2}1\pi^{2}$ (39), $1\sigma2\sigma1\pi^{2}$ (21), $1\sigma^{2}1\pi3\pi$ (10), $1\sigma2\sigma3\pi$ (4)</td>
</tr>
<tr>
<td>$^{3}\Sigma^{+}$</td>
<td>$1\sigma^{2}2\sigma\sigma_{Ry}$ (40), $1\sigma^{2}2\sigma\sigma_{Ry}$ (35), $1\sigma^{2}2\sigma\sigma_{Ry}$ (9)</td>
</tr>
</tbody>
</table>
(4s^25s)^2S Rydberg state while the first excited state of Ge⁺ is a valence (4s^4p^2)^4P state. The excited states of Ge⁺ are also much higher in energy than the excited states of Ga. For example, the first excited state of the Ga (4s^25s)^2S state is only 24 790 cm⁻¹ above the ground state while the corresponding state of Ge⁺ is 61 500 cm⁻¹ above the ground state. Consequently, there are many more low-lying excited states for GaH with 39 000 cm⁻¹ < T_e < 52 000 cm⁻¹ while there is only one state of GeH⁺ in this region. Thus the two species differ significantly in this region.

A notable consequence of much a larger energy separation of the (4s^25s)^2S Rydberg state of Ge⁺ is the absence of a second minimum in the \( ^1\Sigma^+ (\Pi) \) curve which was found for GaH with \( r_e \sim 3.58 \text{ Å} \). This is absent for GeH⁺ as seen from Fig. 1.

It is of interest to compare our predictions on GeH⁺ with the known spectroscopic constants of SiH⁺. Douglas and Lutz (3) have studied the \( A^1\Pi - \chi^1\Sigma^+ \) transition of SiH⁺ through the emission spectrum of a hollow-cathode discharge in helium containing a trace of silane. The analysis of the observed bands provided spectroscopic constants for these states. The \( D_0^0(\text{SiH}^+) \) was deduced to be 3.20 ± 0.08 eV. An ionization potential of 8.01 ± 0.08 eV was deduced for SiH. Rao and Lakshman (5) have obtained the Franck–Condon factors and RKR potential energy curves for SiH⁺. The \( r_e \) of the \( A^1\Pi \) state was found to be ∼0.38 Å larger than the ground state \( r_e \). The \( \omega_e \) of the \( A^1\Pi \) state was found to be only 469 cm⁻¹. Thus the potential energy curve of the \( A^1\Pi \) state of SiH⁺ was found to be shallow.

The above findings for SiH⁺ are fully consistent with our present calculations on GeH⁺. As seen from Table II, the \( r_e \) of the \( A^1\Pi \) state is almost 1.1 Å longer than the \( \chi^1\Sigma^+ \) state. Although we expect the \( A^1\Pi \) state of GeH⁺ to have a longer bond length than SiH⁺, an \( r_e \) value of 2.8 Å is considerably longer, most probably due to the limitations in the basis sets and level of theory. The \( D_0(\text{SiH}^+) \) should be larger than GeH⁺. Hence our predicted value of 2.95 eV is reasonable. The IP of SiH (8.01 eV) should also be larger than our predicted IP of GeH (7.47 eV). Hence our results on GeH⁺ are consistent with known experimental data on SiH⁺.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant CHE8818869. K.K.D. thanks North Bengal University, Darjeeling-734430, India, for providing a leave of absence.

RECEIVED: March 26, 1990

REFERENCES