Analysis of Germanium Hydride Molecular Clusters

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Abstract
Isotope clusters in library electron ionization mass spectra of germanes often appear a few u lower than theoretically expected from elemental composition; for example, the dominant peak of the Ge₄H₁₀⁺ pattern is shifted 8 u down. This phenomenon is due to combinations of three essential components: the molecular ion GeₙH₂n⁺² and two products of hydrogen elimination, Geₙ⁺ and Ge⁺. Using these components, isotope clusters can be accurately projected for germanium hydrides from Ge₂H₆ up to Ge₉H₁₂.

Key words: Germanium hydrides, Molecular clusters, Isotopomeric analysis

Introduction
The mass spectra of organometallic derivatives display, in high abundance, fragment ions that retain the metal element. These ions can be identified due to the distinct isotopic composition of the higher elements that are known to have significant natural abundances. An even more complex pattern often results from ions that differ in chemical composition by only one or two hydrogens [1], as is often the case for compounds containing alkyl groups bonded directly to the metal element. In such cases, the use of high-resolution mass spectrometry and the careful analysis of peak intensities becomes essential in order to fully elucidate the fragmentation patterns. Mass spectrometry seems to be an effective method for the identification and investigation of Ge compound structures due to the characteristic isotopic distribution pattern at 70–76 u. The occurrence of germanium atoms leads to complex isotopomeric clusters in mass spectra and a shift in the most abundant peak in the ionic pattern, particularly for compounds containing more than one germanium atom in the molecule. The location of the most abundant peak of the isotopomeric cluster (LAPIC) [1] is difficult to predict for these ions, especially for species containing several germanium atoms.

Some interesting features of germanium and germanes can be found in the literature. Martin and Schaber [2] obtained the mass spectra of germanium clusters. They found that the intensity of the Geₙ⁺ ion cluster decreases above n = 6 and again above n = 10. Gingerich’s studies [3, 4] of the thermodynamic properties of group IV element clusters provided the atomization energies and enthalpies of formation of Ge₂ to Ge₈. These parameters were obtained from mass spectrometric equilibrium data measurement. Germanium in hydrides was revealed to be not only four-coordinated but to sometimes form only two bonds in linear chain or cyclic structures. The planar digermene H₂Ge = GeH₂ form is the transition state in the interconversion of the germylgermylene H₃Ge–GeH structure, which was found to correspond to minimum enthalpy [5]. Theoretical and experimental investigations [6] indicate that Ge₃ and Ge₄ clusters have cyclic structures. Germanium also forms several compounds with 3D cyclic structures [7, 8], such as tetragermatetrahedrane (Ge₄H₄), hexagermaprismane (Ge₆H₆), octagermacubane (Ge₈H₈), dipentagermaprismane (Ge₁₀H₁₀), octagermaprismane (Ge₈H₈), and polygermanes.

Mass Spectral Features of Germanium Hydrides
The first studies of germanium hydrides were mass spectrometric studies of simple hydrides [9, 10] performed...
by Saalfeld and Svec. Germanium tetrahydride commonly decomposes in the following manner (Equation 1) [11]:

$$\text{GeH}_4 \rightarrow \text{GeH}_3 + \text{H} \rightarrow \text{GeH}_2 + 2\text{H} \rightarrow \text{GeH} + 3\text{H}$$

$$\rightarrow \text{Ge} + 4\text{H},$$

but the complex destruction of GeH$_4$ is also possible via the reaction (Equation 2) [11]

$$\text{GeH}_4 \rightarrow \text{Ge}_2 \rightarrow \text{H}_0 - 3 + \text{yH}.$$

The mass spectra of some higher hydrides such as Ge$_2$H$_6$, Ge$_3$H$_8$ and Ge$_4$H$_{10}$ have also been investigated [10]. Unlike GeH$_4$, the digermane Ge$_2$H$_6$ and subsequent germanes exhibit reasonably intense molecular patterns. The identification of germanes can be a difficult task. The molecular clusters in the EI mass spectra from MS databases (derived experimentally) are located a few u lower than the patterns theoretically expected from expected isotopic abundances of the element isotopes, but the expected and experimental LAPIC parameters are significantly different.

The present work undertakes a theoretical exploration of this question by modeling low-resolution isotopomeric clusters of the germanium hydride molecular ions from Ge$_2$H$_6$ to Ge$_5$H$_{12}$.

Calculations of Molecular Cluster Contents

The theoretical clusters were calculated by the molecular modeling of isotopomeric pattern (MMIP) method [1]. The locations and intensities of peaks were predicted from the formula of the ion and the natural abundances of the element isotopes, but the expected and experimental LAPIC parameters are significantly different.

The experimental molecular ion clusters of Ge$_2$H$_6$, Ge$_3$H$_8$, Ge$_4$H$_{10}$ and Ge$_5$H$_{12}$ were examined by isotopomeric modeling as complex patterns. The shifting of the main peaks suggests that the components are products of dehydrogenation. Shifting values indicate more advanced stages of the process of hydrogen elimination, such as M - H, M - H$_2$, or M - (H$_2$ + H), as can be theoretically predicted [1].

The intensities of experimental peaks $P_{\text{exp},i}$ located within the range $m_1$ to $m_t$ are compared ($P_{\text{exp}} \leftrightarrow P_{\text{calc}}$) with predictions [19] based on the molecular formula of the compound investigated and the corresponding natural isotope abundance (peaks with intensities of $P_{\text{calc},i}$ positioned within the region $m_1$ to $m_k$):

$$m_1 \left[ \begin{array}{c} P_{\text{exp},1} \\ P_{\text{exp},2} \\ P_{\text{exp},3} \\ \vdots \\ P_{\text{exp},t} \end{array} \right] \leftrightarrow \left[ \begin{array}{c} P_{\text{calc},1} \\ P_{\text{calc},2} \\ P_{\text{calc},3} \\ \vdots \\ P_{\text{calc},k} \end{array} \right] m_k$$

$$m_1 \left[ \begin{array}{c} m_1 \\ m_2 \\ \vdots \\ m_{t-2} \\ m_{t-1} \end{array} \right] \leftrightarrow \left[ \begin{array}{c} m_1 \\ m_2 \\ \vdots \\ m_{k-2} \\ m_{k-1} \end{array} \right] m_k$$

The accordance level is estimated from peak intensities by the “theoretical” variance $s^2_{\text{theor}}$, calculated from the number of peaks $v$ that occur simultaneously among both the theoretical and experimental $m/z$ values:

$$s^2_{\text{theor}} = \frac{1}{v} \sum_{i=1}^{v} (P_{\text{exp},i} - P_{\text{calc},i})^2$$

A high value of $s^2_{\text{theor}}$ suggests that further modeling of the molecular pattern region is needed. The procedure
applied is similar to that employed for dehydrogenation [1]; all of the ions in the range from Ge\(_n\)H\(_{2n+2}\) \(^+\) to Ge\(_n^+\) are considered.

The modeling described here deals with compounds of formula Ge\(_n\)H\(_{2n+2}\), and the theoretical vector contains \(k\) elements:

\[
P_{hiw} = \sum_{i=0}^{2n+2} a_i \cdot P_i
\]

where \(w = \) row number

\[
w < 1, \quad 2n + k + 2 >
\]

\[
a_0 \quad a_1 \quad a_2 \quad \cdots \quad a_{(2n)} \quad a_{(2n+1)} \quad a_{(2n+2)} \quad i = < 0, 2n + 2 >
\]

Scheme 2

1. The quasi-molecular cluster [1] is calculated with the aid of a working matrix with of \(2n + k\) 2 rows and \(2n + 3\) columns consisting of the following components:

- The real molecular pattern \(M\) (theoretical band predicted from the formula and natural isotope abundance)
- The first stage of hydrogen radical loss (M – H)
- The second step of hydroge molecule loss (M – 2H)
- The third step (M – 3H), and so on up to \(2n + 2\) components
- The others, respectively.

Each column is filled with the isotopomeric cluster expected by the MMIP method [20] based on element contents and element isotopic abundances. Patterns of neighboring columns are shifted according to the mass of the ion considered. The ion Ge\(_n^+\) is located from the first element (1 \(\rightarrow k\)) in the last column \((2n + 2)\) of the working matrix. The peaks of the molecular ion cluster are placed in the last \((2n + 2 - k \rightarrow 2n + 2)\) elements of the first column (0). Empty elements in the working matrix are filled with zeros. The completed matrix is shown in Scheme 2.

2. The coefficients of the columns \([M, (M – H), (M – 2H), \text{etc.}]\) are \(a_0, a_1, a_2 \ldots \) up to \(a_{(2n+2)}\), respectively. The sum

\[
\sum_{i=0}^{2n+2} a_i = 1
\]

for peaks in the cluster. The matrix is transformed into a vector \((P_{\text{calc.}} \rightarrow P_{\text{exp}})\) by adding all of the terms located in the same row.

3. The predicted pattern mentioned above is finally normalized to 100% \((P_{\text{exp}} \rightarrow P_{\text{model}})\). The experimental intensities are then compared with the intensities of the respective signals of the model \((P_{\text{exp}} \rightarrow P_{\text{model}})\):

\[
m_1 \begin{bmatrix} P_{\text{exp.1}} \\ P_{\text{exp.2}} \\ P_{\text{exp.3}} \\ \vdots \\ P_{\text{exp.} (i-2)} \\ P_{\text{exp.} (i-1)} \\ P_{\text{exp.1}} \end{bmatrix} \leftrightarrow \begin{bmatrix} P_{\text{model.1}} \\ P_{\text{model.2}} \\ P_{\text{model.3}} \\ \vdots \\ P_{\text{model.} (w-3)} \\ P_{\text{model.} (w-2)} \\ P_{\text{model.w}} \end{bmatrix}
\]

Scheme 3

The accordance level is estimated using the model variance \(S_{\text{model}}^2\) calculated for the number \(v\) of peaks that
occur simultaneously in both the theoretical and the experimental bands:

\[ s^2_{\text{model}} = \frac{1}{v} \sum_{i=1}^{v} \left( P_{\text{exp},i} - P_{\text{model},i} \right)^2 \]  

(4)

The part parameters \( a_0, a_1, \ldots \) up to \( a_{2(n+2)} \) of the quasi-molecular pattern model are varied until the minimal value of \( s^2_{\text{model}} \) is reached. The calculations involve predicting the number of components that form the experimental cluster as well as the values of the \( a_i \) factors that describe the ion contributions to the experimental mass cluster. The procedure presented here involves the joint use of numerical and graphical methods, which solves the problem of local minima and simplifies the determination of the quasi-molecular cluster components. The calculation is continued until the smallest possible value of \( s^2_{\text{model}} \) is obtained, and until the best overlap between the model and the experimental clusters is reached. This procedure yields the best agreement of the model with the experimental data. The three-component model is adequate for the elucidation of these mass spectral clusters.

**Discussion**

The relatively small improvement in the adjustment factor \( \alpha \) obtained when the more complex models were used instead of models with three components shows that it is ineffective to use models with more than three components. This fact is highly unexpected. Is the existence of \( \text{Ge}_n^+ \) and \( \text{Ge}_n \text{H}^+ \) ions possible? Are these ions sufficiently stable to be registered in mass spectra?

Features of germanium such as variable valence (II and/or IV), potential for catenation, and the ability to form ions of cyclic and 3D structures may provide the basis for the occurrence of \( \text{Ge}_n^+ \) and \( \text{Ge}_n \text{H}^+ \) ions in experimental mass spectra. Nevertheless, the determination of \( \text{Ge}_n \text{H}^+ \) and \( \text{Ge}_n^+ \) ions in common EI mass spectra is indeed a surprise. The same species can arise in Knudsen effusion mass spectrometry and in standard electron ionization. The calculations presented here indicate that this is actually the case. The electron ionization of simple germanes runs to high levels of dehydrogenation. The results reveal a tendency for the mass spectra of higher hydrides

### Table 1. Modeling of germane quasi-molecular clusters

| Peaks | LAPIC (u) | \( s^2_{\text{theor}} \) | \( s^2_{\text{model}} \) | \( \alpha \) |
|-------|-----------|----------------|----------------|--------|
| Ge\(_2\)H\(_6\) | 14 | 151 | 145 [17] | 1341 | 73 | 82.1 |
| | 27 | 22 | 21 | 57 | 55.4 | 95.9 |
| | 20 | 12 | 11 | 57 | 97.9 |
| | 19 | 8 | 14 | 58 | 98 |
| | 34 | | | | 97.9 |
| Ge\(_3\)H\(_8\) | 25 | 226 | 219 [18] | 2306 | 38 | 37 | 46.0 | 98.0 |
| | 24 | 14 | 14 | 22 | 98.5 |
| | 18 | 3 | 23 | 34 | 99.7 |
| | 25 | | | | 91.6 |
| Ge\(_4\)H\(_{10}\) | 33 | 300 | 292 [19] | 1768 | 27 | 27 | 52 | 10.8 | 99.4 |
| | 18 | 10 | 30 | 42 | 99.5 |
| | 18 | 3 | 10 | 25 | 44 | 99.7 |
| | 23 | 7 | 24 | 46 | 99.8 |
| | 17 | 4 | 11 | 26 | 42 | 99.8 |
| | 20 | 1 | 2 | 10 | 23 | 44 | 99.9 |
| Ge\(_5\)H\(_{12}\) | 37 | 376 | 364 [20] | 1972 | 19 | 8 | 28 | 55 | 10.0 | 99.5 |
| | 16 | 7 | 28 | 49 | 99.9 |
| Ge\(_n\)H\(_{2n+2}\) | | | \( \text{Ge}_n^+ \) | | | | | | |
to be dominated by the ions with the highest germanium content, resulting from the complete elimination of hydrogen.

These results illustrate how many new possibilities can be realized through the systematic mathematical analysis of mass spectra. It is hoped that the application of isotopomeric analysis will enable the disclosure of many scientific secrets hidden in electron ionization mass spectra.

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