Towards Detection of a Long-lived Protonated Metal Cation: Generation of GeH^{2+} Using High-Energy Collisions**

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Dedicated to Rolf Huisgen
on the occasion of his 80th birthday

Multiply charged ions are a topic of interest in biochemistry and chemical physics.[1, 2] Recently, thermochemically stable diatomic trications have been synthesized by using the technique of charge-stripping mass spectrometry.[3, 4] For a diatomic di- or trication AB^{n+} to be classified as thermochemically stable, the polycationic minimum must lie below the asymptotes of the charged separated products $A^{(n-1)+} + B^+$; otherwise electronic rearrangement can lead to repulsive dissociation via the Coulomb asymptote. Metastable dications, in which this latter situation holds, may survive long enough to be detected in microsecond time scale (or shorter) experiments. To date, most of the diatomic trications synthesized possess halogen ligands;[1–7] electrostatic complexes of multiply charged metals with rare gas ligands should also be feasible,[8, 9] but only few of them, for example VHe^{3+}, have been reported.[10]

Considerable controversy surrounds the proposed detection of CH^{2+},[11–15] and very recent experiments refute its existence.[16] Calculations do however suggest that long-lived $^2\Sigma^+$ CH^{2+} may be detectable, provided it is possible to generate this ion at all, as poor Franck–Condon factors render its generation from CH^+ in charge-stripping experiments almost impossible. Another problem associated with the detection of CH^{2+} is the non-negligible abundance of ^{13}C, and in some reports this source of artefact has not been adequately addressed. Similar problems were encountered during the characterization of $^{28}SiH^{2+}$ [17] as this ion is isobaric with the ^{29}Si isotope.

In this study, we present the first unambiguous evidence for the existence of GeH^{2+}, a metastable, protonated metalloid cation.[18] To characterize the bonding and stability of this particular ion, calculations at the CCSD(T)/cc-pVTZ level of theory have been used to map the potential-energy surface.[19] On the basis of similar theoretical results, the previously suggested[17, 20] existence of metastable SiH^{2+} is also confirmed.

The charge-stripping mass spectrum of $^{70}GeH_2^+$ (m/z 10 to m/z 69) is presented in Figure 1. The overwhelmingly abundant singly charged dissociation products m/z 70 and 71 (loss of H_n, $n = 1,2$) were not recorded. The peak at m/z 35 is due to $^{70}Ge^{2+}$, while the peak at m/z 36 could be a mixture of isobaric $^{72}Ge^{2+}$ and $^{70}GeH_2^{2+}$. Except the contribution of ^{72}Ge, no other isobaric impurities were observed, in particular, as there exists no ^{71}Ge isotope, the peak at m/z 35.5 is unequivocally $^{70}GeH^{2+}$. On the basis of this spectrum, GeH^{2+} is stable at least on a microsecond time scale.

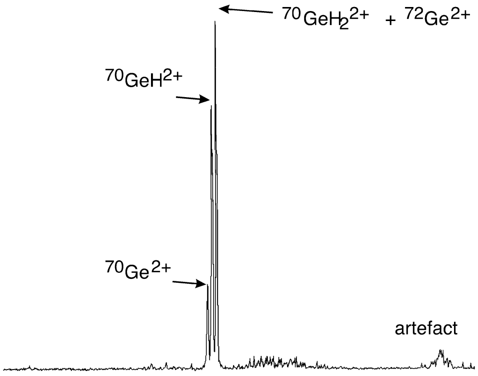

Figure 1. Charge-stripping mass spectrum of $[^{70}Ge,H_2]^+$, containing some $^{72}Ge^+$, with O_2 as the target gas.

Modeling of the $[Ge,H_2]^+$ potential-energy surfaces, to be reported in greater detail in a follow-up publication,[21] provides a simple rationale for the generation of GeH^{2+} from this precursor in collision experiments. The reason becomes clear on inspection of the bond lengths calculated by density functionl theory (DFT) (Table 1). The bond lengths of the diatomics GeH^+ and GeH^{2+} differ substantially (41.8 pm). While charge stripping of the GeH^+ monocation affords a tiny

Table 1. Energy E, Ge–H distance R_e, H-Ge-H angle θHGeH, and vibrational frequency ωe of small neutral and ionic germanium hydride species calculated at the B3LYP/6-311++G(d,p) level. The normal mode symmetry is given in parentheses.

	E [Hartree]	R_e [pm]	θ_{HGeH} [°]	ω_e [cm^{-1}]
$^2\Pi$ GeH[a]	–2077.52295	159.8		1812
$^1\Sigma^+$ GeH^+[a]	–2077.25461	159.2		1944
$^3\Pi$ GeH^+[a]	–2077.16816	169.5		1267
$^2B_2$ $Ge(H_2)^+$	–2077.81284	218.5	20.3	406 (a_1) 625 (b_1) 3994 (a_1)
$^2A_1$ $HGeH^+$	–2077.81096	154.8	120.3	817 (a_1) 2021 (a_1) 2109 (b_1)
$^2\Sigma^+$ GeH^{2+}	–2076.58479	201.0		606

[a] Values taken from ref. [37]. The frequencies were evaluated by using a valence basis set of double-zeta plus quality and effective core potential (ECP).[38, 39]

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dication signal due to GeH^{2+}, vertical ionization might therefore cause dissociation of the dication. In contrast, the Ge–H bond lengths of the $[Ge,H_2]^+$ global minimum, $^2B_2$ $Ge(H_2)^+$, are much closer to the calculated dication value. It is then possible to envisage formation of GeH^{2+} as a concerted charge-stripping/bond-fission event resulting from a small-impact parameter, impulsive collision between the target gas and $Ge(H_2)^+$ generated in the ion source. The low dication yields compared with singly charged collisional-activation products suggest that interactions with electrophilic dioxygen at 8 kV result primarily in simple bond cleavages, and collisions yielding the dications are disfavored (small cross-section).

The results from the coupled-cluster investigations of XH^{2+}, X = Si, Ge, are presented in Table 2 and Figure 2. Except for the Ge–H bond lengths in the dication, the CCSD(T) and B3LYP data agree quite well. Inspection of the heats of reaction reveals the Coulomb explosion asymptotes, $X^+ + H^+$, are below the stationary points located for the dications, indicating the XH^{2+} dications are metastable for both elements. The zero-point corrected bond strength $D(Si^{2+}–H)$ is 1.16 eV (26.9 kcal mol^{-1}),[22] whereas for Ge the Ge^{2+}–H bond is slightly weaker at 0.93 eV (21.7 kcal mol^{-1}). For both dications, the ground states are $^2\Sigma^+$, and the bonds between X and H can be described as one-electron sigma bonds, with hydrogen the principal electron donor. At the B3LYP level,[23] the Mulliken atomic charges are +1.68 (Si) and +0.32 (H) and +1.70 (Ge) and +0.30 (H), which supports a localized bonding model $X^{2+}(4s^2 4p^0)–H(1s^1)$. The B3LYP spin densities, +0.49 (Si) and +0.51(H) and +0.37 (Ge) and +0.63 (H), infer a much larger degree of HOMO polarization towards the H atom for GeH^{2+}, but both spin distributions implicate H-electron donation to the superacid X^{2+} as the source of molecular stabilization.

Table 2. CCSD(T)/cc-pVTZ results for H, X^{n+}, $n = 0–2$, and XH^{n+}, $n = 1,2$, X = Si, Ge (T_e = term energy).

	Term	E [Hartree]	R_e [pm]	T_e [eV]
H	^2S	−0.499810		
Si	^3P	−288.986846		
Si^+	^2P	−288.689336		
Si^{2+}	^1S	−288.093388		
SiH^+	$^1\Sigma^+$	−289.313174	150.9	0.0000
SiH^{2+}	$^2\Sigma^+$ ($3p_z$)	−288.637650	174.3	18.3821
	$^2\Pi$ ($3p_x$)	−288.496015	183.1	22.2362
	$^4\Pi$ ($3sp_zp_x$)	−288.405045	209.9	24.7116
Ge	^3P	−2075.549500		
Ge^+	^2P	−2075.259788		
Ge^{2+}	^1S	−2074.683559		
GeH^+	$^1\Sigma^+$	−2075.877059	156.8	0.0000
GeH^{2+}	$^2\Sigma^+$ ($4p_z$)	−2075.219026	189.3	17.9061
	$^2\Pi$ ($4p_x$)	−2075.062057	191.9	22.1775
	$^4\Pi$ ($4sp_zp_x$)	−2074.962485	216.1	24.8870
$SiH^+ \rightarrow Si^+ + H$			3.3750[a]	
$SiH^{2+} \rightarrow Si^{2+} + H$			1.2096[a]	
$SiH^{2+} \rightarrow Si^+ + H^+$			−1.4065[a]	
$GeH^+ \rightarrow Ge^+ + H$			3.1963[a]	
$GeH^{2+} \rightarrow Ge^{2+} + H$			0.9703[a]	
$GeH^{2+} \rightarrow Ge^+ + H^+$			−1.1092[a]	

[a] Zero Kelvin reaction enthalpy in eV.

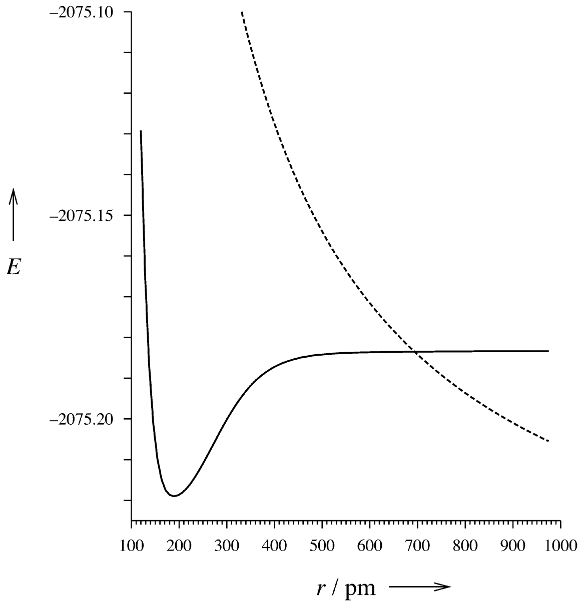

Figure 2. Potential-energy surface scan of GeH^{2+} (solid line). Absolute CCSD(T)-Energy E is given in Hartree. Dashed line represents Coulomb repulsion, $E(r) = E(Ge^+) + E(H^+) + 1/r$.

Spin-orbit corrections for the bond strengths of the dications are zero, as all the species involved are either closed-shell or $m_l = 0$; the only exception is the $^2X^+ + {}^1H^+$ asymptote, for which empirical spin-orbit-weighted-average corrections of 0.55 kcal mol^{-1} [24] and 3.37 kcal mol^{-1} [25] can be used to adjust the surfaces for $^2P_{1/2}/^2P_{3/2}$ X^+, X = Si, Ge, respectively.

We present the uncorrected and spin-orbit-corrected atomic ionization energies (first and second for Si and Ge) calculated at the B3LYP/6-311++G(d,p) and CCSD(T)/cc-pVTZ levels of theory in Table 3. We have also tabulated the experimental values for comparison; the energy levels for the ground state terms of Si^0/Si^+ and Ge^0/Ge^+ are given in Table 4. The coupled-cluster results are clearly superior, but this may be attributable to the saturated nature of the larger basis set used in these calculations, so B3LYP with a modest triple-zeta basis set performs adequately in this regard.

Table 3. Atomic ionization energies (IE) in eV calculated at the B3LYP/6-311++G(d,p) and CCSD(T)/cc-pVTZ level. The numbers in parentheses are spin-orbit corrected according to the values in Table 4. The final row gives the mean variance[a] in the experimental and theoretical ionization energies.

	Atom	B3LYP	CCSD(T)	Exp.
IE(X)[b]	H	13.667	13.601	13.598[d]
	Si	8.113 (8.108)	8.096 (8.091)	8.152[e]
	Ge	7.831 (7.805)	7.884 (7.858)	7.899[f]
IE(X^+)[c]	Si	16.397 (16.421)	16.217 (16.241)	16.345[e]
	Ge	15.424 (15.570)	15.680 (15.826)	15.934[f]
mean variance[a]		0.104 (0.078)	0.058 (0.033)	

[a] Calculated as $(\Sigma(IE_{calcd} - IE_{exp})^2)^{1/2}/N$. [b] For X = H, the transition is ^2S H → ^1S H^+; for X = Si, Ge, ^3P X → ^2P X^+. [c] The transition is ^2P X^+ → ^1S X^{2+}; X = Si, Ge. [d] Ref. [40]. [e] Ref. [24]. [f] Ref. [25].

To conclude, it is quite remarkable that GeH^{2+} was even detected in our experiments, given that the ionization energy

Table 4. J-level energies (E_J) and corresponding weighted average[a] in eV for Si atoms and Si^+ ions[24] as well as for Ge atoms and Ge^+ ions.[25]

Level	Si	Ge	Level	Si^+	Ge^+
$^3P_0$	0.00000	0.00000	$^2P_{1/2}$	0.00000	0.00000
$^3P_1$	0.00956	0.06908	$^2P_{3/2}$	0.03561	0.21912
$^3P_2$	0.02767	0.17481			
weighted average[a]	0.01856	0.12014		0.02374	0.14608

[a] Weighted average, calculated as $\dfrac{\sum_{J_{\min}}^{J_{\max}}(2J+1)E_J}{(2L+1)(2S+1)}$

of hydrogen is 2.34 eV less than the second ionization energy of Ge ($^2P\ Ge^+ \rightarrow {}^1S\ Ge^{2+}$); this implies that exothermic internal conversion and dissociation via $^2Ge^+ + {}^1H^+$ must be significantly barrier-hindered (Figure 2), as the ion has sufficient time for many thousands of vibrations after formation. Our results for SiH^{2+} also support the previous assignments and $Q_{\min}$ value ($Q_{\min}$ = kinetic energy loss in CS) measured by Porter et al.;[20] the lower experimental value reported by Koch et al.[17] appears to be due to interfering $^{29}Si^+$. Compared to GeH^{2+}, the silicon hydride dication will be shorter lived on account of the greater covalency of the SiH^{2+} bond. The greater covalency of the Si^{2+}–H bond entails the hydrogen electron residing closer to the Si^{2+} fragment. Thus, the $Si^+ + H^+$ configuration must make a greater contribution to the ground-state wavefunction. A natural consequence of this will be that internal conversion must be more probable for this ion.

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[18] The charge-stripping of $^{70}GeH_2^+$, generated by the chemical ionization of GeH_4, was performed using an instrument of BEBE configuration (B represents magnetic and E electric sector) which has been described in detail in a number of articles.[26, 27] The experiments were conducted as follows: $^{70}GeH_2^+$ was mass-selected by using B(1)E(1) at a mass resolution of $m/\Delta m \approx 3000$, and collided with stationary O_2 molecules at 8 kV. The O_2 pressure was maintained so that the ions traversing the collision cell undergo an average of 1.0–1.2 collisions.[28] This results in both collisional dissociation and charge-stripping events, leading to the generation of small amounts of $^{70}GeH^{2+}$ (m/z 35.5). Fortuitously, there is no ^{71}Ge isotope, however we are left to speculate about the existence of $^{70}GeH_2^{2+}$ because of isobaric interference from $^{72}Ge^{2+}$ (see below).

[19] The ground-state geometries of GeH_n^+ (n = 1,2) and GeH^{2+}, as presented in Table 1, were calculated by using B3LYP in conjunction with triple-zeta basis sets[29, 30] and the Gaussian 94 suite of programs.[31] Coupled-cluster calculations with perturbative triples (CCSD(T)) and correlation-consistent triple-zeta basis sets of Dunning,[32–34] were used to refine the energetics for GeH^{2+} and established the stability of SiH^{2+}. MOLPRO 96[35, 36] was used for these calculations. The frozen-core approximation was used to exclude the n = 1 shell of Si, and n = 1,2 shells of Ge, from the expansion with negligible cost to the accuracy of the results. The calculations were carried out on a Cray-YMP supercomputer housed at the Konrad-Zuse-Zentrum für Informationstechnik, Berlin.

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