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Stability of Ligand Free Germanium–Gold Clusters

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The recognition of the key role which small anatomic and molecular metal clusters play in homogeneous nucleation and crystal growth [1], photographic systems [2], and heterogeneous catalysis [3], has caused extensive experimental and theoretical study of such systems over the last decade.

We have been engaged in the mass spectrometric determination of the stability of polyatomic metals such as tin molecules [4] and have recently measured the atomization energies of the first intermetallic ligand free transition metal containing molecules with four atoms, Au_2Sn_2 and $AuSn_3$ [5]. We have since extended the study of ligand free intermetallic clusters to germanium-gold molecules containing up to five atoms and report here their stability.

The Knudsen-cell mass spectrometer and procedure used in the present investigation has been previously described [6, 7]. The sample consisted of a 0.49–0.49–0.02 molar ratio Au–Ge–Cu alloy, contained in a graphite liner that was inserted in a tantalum effusion cell. Measurements were performed over a 1466 - 2063 °K temperature range. A typical set of relative ion currents measured with 20 eV electrons at 1947 °K is given [8]: Au^+, 1.19×10^{-7}; Au_2^+, 1.99×10^{-10}; Ge^+, 1.77×10^{-7}; Ge_2^+, 1.84×10^{-9}; Ge_3^+, 2.45×10^{-10}; Ge_4^+, 3.96×10^{-11}; $AuGe^+$, 1.18×10^{-8}; $AuGe_2^+$, 9.03×10^{-11}; Au_2Ge, $\sim 8 \times 10^{-11}$; Au_2Ge_2, 6.36×10^{-13}; $AuGe_3$, 2.10×10^{-12}; $AuGe_4$, 6.90×10^{-13}; Cu^+, 2.90×10^{-8}; $AuCu^+$, 1.46×10^{-10}; $CuGe^+$, 2.06×10^{-11}; $CuGe_2^+$, 1.85×10^{-12}.

The atomization energies, D°_{298} (in kJ mol^{-1}) of 273.4 ± 5, 539 ± 12 and 536 ± 8 of the molecules AuGe, $AuGe_2$, and Au_2Ge, respectively have been derived from the measured second and third law enthalpies of various reactions. These selected values for $AuGe_2$ (asymmetric) and Au_2Ge (symmetric) correspond to the assumed bent structures, that appear to be preferred on the basis of better second and third law agreement and smaller standard deviation of the third law results.

For the molecules Au_2Ge_2, $AuGe_3$ and $AuGe_3$, only third law evaluations could be performed, which are summarized in Table I for the different structures considered, together with the corresponding atomization energies. Thus the strong influence on the choice of structure is also demonstrated. No decision concerning the structure on the basis of our data alone can be made and the need for optical spectroscopic measurements, *e.g.* using matrix isolation techniques, is apparent.

The errors given in Table I for the reaction enthalpies correspond to the standard deviation (or deviation from the arithmetic mean in case of $AuGe_4$). Those given for the atomization energies correspond to estimated overall errors assuming the correct geometry.

The bond energies measured in this investigation for the germanium-gold molecules are generally similar to those expected from bond additivity concepts if compared with that for Au_2 and the germanium molecules Ge_2, Ge_3, and Ge_4, for the latter of which the atomization energies ($D^\circ_{a,298}$, in

TABLE I. Third-law Reaction Enthalpies Measured between 1934 °K and 2063 °K and Derived Atomization Energies of Au_2Ge_2, $AuGe_3$ and $AuGe_4$.

Reaction	No. of Data Sets	$-\Delta[(G^\circ_T - H^\circ_{298})/T]$ J K^{-1}	ΔH°_{298} 3rd Law kJ	$D^\circ_{a,298}(M)^a$ kJ mol^{-1}	M	Assumed Structure of M
$Au_2Ge_2(g) = 2AuGe(g)$	6	45.3	388.6 ± 2.8	935.4 ± 14	Au_2Ge_2	Lin.
	6	36.4	313.8 ± 3.5	860.6 ± 18		Sq. Pl.
	6	39.3	338.7 ± 3.2	885.5 ± 16		Tetrah.
$AuGe_3(g) + 2Au(g) = 3AuGe(g)$	7	20.2	85.4 ± 2.5	905.6 ± 13	$AuGe_3$	Lin.
	7	18.8	75.3 ± 2.6	895.5 ± 13		Tetrah.
$AuGe_4(g) + 3Au(g) = 4AuGe(g)$	2	37.4	158.7 ± 4.9	1252.3 ± 25	$AuGe_4$	Lin.
	2	50.2	216.4 ± 4.5	1309.7 ± 23		Trig. BiPyr.
	2	32.9	140.6 ± 5.0	1234.2 ± 25		Tetrah.

^{a}Using D°_{298} [AuGe(g)] = 273.5 ± 5 kJ mol^{-1}, this investigation.

kJ mol^{-1}) corresponding to the linear structure have been determined as 269.2 ± 10, 633.3 ± 20 and 971.1 ± 22, respectively, in the present investigation.

The high experimental values measured for the bond energies of the polyatomic germanium–gold molecules could be accounted for by linear molecules with multiple bonds between the germanium atoms and polar covalent single bonds between germanium and gold, or by cluster molecules containing a larger number of presumed single bonds. For the molecule Sn_5, Anderson [9] demonstrated on the basis of theoretical calculations that the trigonal bipyramidal form is probably the most stable one. The same may be assumed for Ge_5, and by extention for $AuGe_4$ investigated here.

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