GASEOUS METAL SILICIDES. II. THERMODYNAMIC STUDY OF THE MOLECULES AuSi, AuSi$_2$ AND Au$_2$Si WITH A MASS SPECTROMETER*

K. A. GINGERICH, R. HAQUE AND J. E. KINGCADE, JR.

Department of Chemistry, Texas A & M University, College Station, Texas 77843 (U.S.A.)

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ABSTRACT

The gaseous equilibria involving the molecules AuSi, AuSi$_2$ and Au$_2$Si have been studied by means of the Knudsen effusion technique combined with mass spectrometric analysis of the vapor. The experimentally determined reaction enthalpies were combined with appropriate literature data to obtain the following atomization energies (in kJ mole^{-1}): D_0^0[AuSi(g)] $=$ 301.0 $\pm$ 6.0, D_0^0[Au$_2$Si(g)] $=$ 582.7 $\pm$ 15 and D_0^0[AuSi$_2$(g)] $=$ 602.1 $\pm$ 15. The corresponding D_{298}^0 values are: 305.2 $\pm$ 6.0, 589.1 $\pm$ 15 and 610.5 $\pm$ 15, and the standard heats of formation, $\Delta H_{f,298}^0$, 518.6, 602.9 and 668.9, respectively.

Comparison of the atomization energies of these silicon–gold molecules with the literature values for the corresponding germanium–gold and tin–gold molecules indicates similarity in the nature of the bonding.

INTRODUCTION

High temperature Knudsen cell mass spectrometry is an acknowledged useful tool in thermodynamic studies on diatomic and polyatomic molecules. For diatomic compounds of gold, for example, while methods like thermal emission and absorption spectroscopy provide information on the electronic energy levels and in favorable cases, on bond lengths, the dissociation energies determined by this method are important in deciding on the nature of the bonding involved[1,2].

The present investigation was undertaken to obtain experimental data on polyatomic gold silicides. Thermodynamic data on polyatomic metal silicides are scarce[1]. The only reported values are for the gaseous molecules AlSi$_2$[3] and Li$_2$Si$_2$[4].

There remained also a discrepancy in the experimentally determined atomization energy of AuSi(g)[5,6]. We have therefore endeavored to determine the atomization energy of this molecule over an extended temperature range. The more recently published experimental optical spectroscopic study by Houdart and Schamps[7] is

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employed in the determination of the atomization energy of AuSi(g).

The following is thus a report of a selected atomization energy of AuSi(g) and the first reported identification and evaluation of the atomization energy of $Au_2Si(g)$ and $AuSi_2(g)$. The values reported here, including those on the previously unknown molecules Au_2Si and $AuSi_2$, might then help in allowing some insight into the nature of the bonding and the structure of these gaseous molecules.

EXPERIMENTAL

A 12-in radius 90° sector high temperature mass spectrometer similar to one described previously[8] was used to carry out the present investigations.

The experiments consisted of two separate runs. In one run the sample consisted of Au, Si, Sc and Cu mixed in the molar ratio $1.00:1.00:0.38:0.27$. Here the copper and scandium were added in order to test also the existence of the not yet known molecules ScSi, ScCu and CuSi. These species could not be identified in careful search whereas the previously known molecules AuCu and ScAu were observed.

The other run had only gold and silicon mixed in the ratio $1.85:1.00$ molar concentration. The pure gold–silicon system gave high intensities of these atoms in the gas phase and facilitated the detection of the triatomics, $AuSi_2(g)$ and $Au_2Si(g)$, before excessive blockage of the cell orifice terminated the run prematurely.

A tantalum cell with a graphite liner with concentric orifices of 0.04 in. diameter was used in both runs. The cell was heated by radiation from a tungsten heater. The temperature was measured with a calibrated Leeds and Northrup optical pyrometer by sighting into a blackbody hole at the bottom of the outer cell. Experimentally determined window and prism corrections were applied.

The ion source used employed magnetic focusing of the electron beam to enhance sensitivity. The neutrals were ionized with electrons of 19 eV energy. For silicon an electron energy of 13 eV was used to minimize background effect of molecular nitrogen. The ions were identified from their mass to charge ratio, shutterability of the peak and their appearance potentials.

RESULTS AND DISCUSSION

Dissociation energy of AuSi

The pressure constant k_{Au} that relates the gold ion current to corresponding partial pressure according to the relation $P_{Au} = k_{Au}I_{Au}^+T$ was evaluated in run I, using the Au–Si–Sc–Cu alloy, from gold monomer–dimer equilibrium ion currents according to the method described by Grimley[9].The necessary Gibbs energy functions for Au were taken from Hultgren et al.[10] and those of Au_2 from Kordis et al.[11], together with the dissociation energy of gold dimer $D_0^0 = 221.3 \pm 2.1$ kJ mole^{-1}.

The pressure constant k_{Au} was evaluated at six temperatures resulting in an

TABLE 1

EXPERIMENTAL AND ESTIMATED PARAMETERS OF SPECIES OVER Au–Si–Sc–Cu-SYSTEM[a]

Ion	Appearance potential (eV)	Ionization cross-section $\sigma_i(A^2)$	Relative multiplier gain γ_i/γ_{Au} ($\gamma_{Au} = 8.70 \times 10^4$)	Intensity correction factor E_i	Calibration constant k_i (atm $A^{-1}K^{-1}$)
Au^+	9.22[b]	5.85	1.00	1.00	0.384
Au_2^+	9.4 ± 0.5	8.78	1.00	1.06	0.272
Si^+	8.2 ± 0.5	5.35	1.72	1.40	0.247
$AuSi^+$	7.8 ± 0.5	7.84	1.00	1.40	0.291
Al^+	6.0 ± 0.5	6.18	1.96	2.04	0.378
$AuAl^+$	7.5 ± 0.5	8.42	1.00	1.83	0.488

[a] See text for details.
[b] Used as reference to correct the electron energy scale. R. W. Kiser, *Introduction to Mass Spectrometry and Its Applications*, Prentice-Hall, Englewood Cliffs, N.J., 1965.

TABLE 2

ION INTENSITIES USED IN THE THERMODYNAMIC EVALUATION OF THE MOLECULE AuSi (IN A)

Set	Temp	$I_{(Au^+)}$	$I_{(Au_2^+)}$	$I_{(Si^+)}$	$I_{(AuSi^+)}$	$I_{(Al^+)}$	$I_{(AlAu^+)}$
1	1672	3.20E-09	1.23E-12	1.25E-12	1.50E-13	9.45E-11	3.72E-11
2	1677	3.90E-09	1.38E-12	3.20E-12	2.70E-13	7.20E-11	1.90E-11
3	1703	6.30E-09	2.85E-12	1.19E-11	9.60E-13	8.00E-11	1.80E-11
4	1743	7.20E-09	3.40E-12	2.40E-11	1.71E-12	7.60E-11	1.50E-11
5	1745	5.20E-09	1.83E-12	3.90E-11	1.10E-12	2.80E-11	3.30E-12
6	1758	7.00E-09		5.70E-11	2.10E-12	2.70E-11	3.40E-12
7	1881	1.26E-09		8.70E-11	2.40E-13		
8	1897	1.17E-09		9.90E-11	2.10E-13		
9	1965	1.17E-09		2.58E-10	3.90E-13		
10	1986	1.05E-09		3.60E-10	4.50E-13		
11	1996	1.17E-09		3.50E-10	3.60E-13		
12	2012	1.08E-09		1.41E-09	7.50E-13		
13	2049	1.11E-09		1.86E-09	9.00E-13		
14	2070	1.17E-09		2.25E-09	9.00E-13		
15	2096	1.17E-09		2.70E-09	1.08E-13		

average value of 0.384 ± 0.006 atm K^{-1} amp^{-1}. Pressure constants for other species were evaluated using the relationship

$$k_i = k_{Au} \frac{E_i \, \sigma_{Au} \, \gamma_{Au} \, \eta_{Au}}{E_{Au} \, \sigma_i \, \gamma_i \, \eta_i}$$

where σ, γ, η represent the maximum ionization cross-section, multiplier efficiency and the isotope factor, respectively. The empirical correction factor E converts experi-

mental ion currents into those corresponding to maximum ionization. The ionization cross-sections were taken from Mann[12]. For molecules the ionization cross-sections were taken as the sum of the atomic cross-sections multiplied by a factor of 0.75[13]. In the absence of accurate measurements it was assumed that $\gamma_{AuSi} = \gamma_{AuAl} = \gamma_{Au_2} = \gamma_{Au}$. Table 1 presents the appearance potential, relative multiplier gain, empirical correction factor and the pressure constants for the species utilized in the evaluation. The presence of Al^+ and $AlAu^+$ was due to apparent impurities in the sample. Table 2 lists the measured ion intensities corresponding to the major isotopes.

The following gas phase reactions were considered

AlAu	$= Al + Au$	(A)
$AlAu + Si$	$= AuSi + Al$	(B)
$Au_2 + Si$	$= AuSi + Au$	(C)
AuSi	$= Au + Si$	(D)

Third law method evaluation according to the relation $\Delta H_0^0 = -RT\ln k - T\Delta[(G_T - H_0^0)/T]$ gives $\Delta H_0^0 = 324.5 \pm 2.1$ kJ mole^{-1} for reaction A. This reaction enthalpy represents the dissociation energy, $D_0^0(AuAl)$, and is to be compared with $D_0^0(AuAl) = 322.2 \pm 6.3$ kJ mole^{-1} as evaluated by Gingerich and Blue[14].

TABLE 3

THIRD LAW EVALUATIONS FOR THE REACTIONS

AlAu(g) + Si(g) = AuSi(g) + Al(g)
and Au₂(g) + Si(g) = AuSi(g) + Au(g)
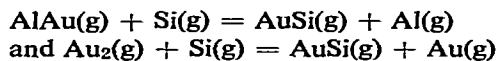
Reaction	T(K)	$-\Delta G_T^0/T$ (J K^{-1} mole^{-1})	$-\Delta[(G_T^\circ - H_0^0)/T]$ (J K^{-1} mole^{-1})	3rd law ΔH_0^0 (kJ mole^{-1})
AlAu(g) + Si(g) = AuSi(g) + Al(g)	1642	10.642	4.810	25.4
	1677	10.245	4.836	25.3
	1703	9.293	4.855	24.1
	1743	9.236	4.884	24.6
	1745	12.654	4.886	30.6
	1758	10.984	4.895	27.9
			Average	26.3 ± 2.3
			D_0^0 (AuSi)	295.9 ± 2.3
Au₂(g) + Si(g) = AuSi(g) + Au(g)	1642	51.989	2.878	80.6
	1677	49.748	2.900	78.6
	1703	47.33	2.915	75.6
	1743	45.943	2.936	75.0
	1758	45.375	2.943	74.6
			Average	75.9 ± 3.1
			D_0^0 (AuSi)	297.2 ± 3.1

Table 3 shows the third law evaluation of reaction B.

$$\Delta H_0^0 = 26.3 \pm 2.3 \text{ kJ mole}^{-1}$$

Combined with the literature value of the dissociation energy $D_0^0(\text{AlAu}) = 322.2 \text{ kJ mole}^{-1}$, this gives $D_0^0(\text{AuSi}) = 295.9 \pm 2.3 \text{ kJ mole}^{-1}$.

Table 3 presents also the third law evaluation of reaction C giving
$$\Delta H_0^0 = 75.9 \pm 3.1 \text{ kJ mole}^{-1}$$

Combining this reaction enthalpy with $D_0^0(\text{Au}_2) = 221.3 \text{ kJ mole}^{-1}$ from Kordis et al.[11], leads to the value $D_0^0(\text{AuSi}) = 297.2 \pm 3.1 \text{ kJ mole}^{-1}$.

Because of the small temperature range (1642–1756 K) together with the limited amount of data involved, the second law evaluations of these reactions are less reliable and are not presented here.

For reaction D, more numerous data over a considerable temperature range (1642–2096 K) could be measured to provide a reliable second law check, using the relation $\ln K = -\Delta H^0/(RT) + \Delta S^0/R$.

Table 4 presents the third law evaluation of reaction D. The summary of the third and second law evaluation for reaction D follows.

3rd law $\Delta S_{298} = 91.3 \text{ J mole}^{-1} \text{ K}^{-1}$
2nd law $\Delta S_{298} = 90.0 \pm 6.5 \text{ J mole}^{-1} \text{ K}^{-1}$

TABLE 4

THIRD LAW EVALUATION FOR THE REACTION

AuSi(g) = Au(g) + Si(g)

T K	$-\Delta G_T^0/T$ $(J\ K^{-1}\ mole^{-1})$	$-\Delta[(G_T^0 - H_0^0)/T$ $(J\ K^{-1}\ mole^{-1})$	3rd law ΔH_0^0 $(kJ\ mole^{-1})$
1642	92.753	91.296	302.3
1677	88.004	91.401	300.9
1703	83.515	91.475	298.1
1743	81.179	91.574	301.0
1745	76.171	91.578	292.7
1758	75.858	91.609	294.4
1881	68.003	91.875	300.7
1897	66.365	91.909	300.2
1965	63.255	92.063	305.2
1986	62.486	92.115	307.0
1996	59.923	92.141	303.5
2012	55.039	92.183	296.2
2049	53.873	92.298	299.5
2070	51.768	92.355	298.3
2096	51.664	92.443	302.0
		Average:	300.2 ± 3.7

TABLE 5

RE-EVALUATION OF THE LITERATURE DATA OF AuSi

Property	Vander Auwera-Mahieu et al.[5]	Gingerich[6]	Present work
D_0^0 (Au$_2$), kJ mole^{-1}	222 2	217.6	221.3
D_0^0 (AlAu), kJ mole^{-1}		322.2	322.2
fef (Au$_2$) 1800, J mole^{-1}K^{-1}	299.4	306.4	299.4
fef (AlAu) 2000, J mole^{-1}K^{-1}		285.3	285.0
fef (AuSi) 1800, J mole^{-1}K^{-1}	289.2	287.0	289.6
D_0^0 (AuSi), kJ mole^{-1}, 2nd Law	300.1		
3rd Law	307.8	318.0	
D_0^0 (AuSi), kJ mole^{-1}, 2nd Law	299.2		
(re-evaluated) 3rd Law	306.2	309.2	

$$\text{3rd law } \Delta H_0^0 = 300.2 \pm 3.7 \text{ kJ mole}^{-1}$$
$$\text{2nd law } \Delta H_0^0 = 297.3 \pm 12.2 \text{ kJ mole}^{-1}$$

The literature value of D_0^0(AuSi) by Gingerich[6] has been re-evaluated using the revised free energy functions for gaseous AuSi of the present investigation that have been based on the results of the optical spectroscopic study by Houdart and Schamps[7]. The literature values have been further adjusted using D_0^0(Au$_2$) $= 221.3 \pm 2.1$[11] and D_0^0(AlAu) $= 322.2 \pm 6.3$ kJ mole^{-1} [14] (see Table 5).

These revised literature values of D_0^0(AuSi) are (kJ mole^{-1})

306.2 $\pm$ 12 by 3rd law method[5] (307.8 $\pm$ 12)

299.2 $\pm$ 12.0 by 2nd law method[5] (300.1 $\pm$ 12)

309.2 $\pm$ 16.7 by 3rd law method[6] (318.0 $\pm$ 16.7)

where the original literature values are shown in parentheses. Here the 2nd law enthalpy by Vander Auwera-Mahieu et al.[5] for reaction C, $\Delta H_0^0 = -77.9 + 12$ kJ mole^{-1} has been combined with the D_0^0(Au$_2$) value of 221.3 $\pm$ 2.1 kJ mole^{-1}.

Gingerich[6] used reactions B and C to evaluate D_0^0(AuSi). With the free energy functions then used, the differences in the values derived came out as 18.4 kJ mole^{-1}. It is of interest to note that with the new free energy functions incorporated, the difference is narrowed down to 2.3 kJ mole^{-1}.

For reasons of prudence, we have given equal weight to all the four values obtained in the present experiment and to the three of the literature values cited above and one-third weight to the single literature value based on reaction B, yielding the selected value of D_0^0(AuSi) as 301.0 $\pm$ 6.0 kJ mole^{-1} or 71.9 $\pm$ 1.4 kcal mole^{-1} (see Table 6). The corresponding value with respect to 298 K reference temperature is 305.2 $\pm$ 6.0 kJ mole^{-1} or 72.9 $\pm$ 1.4 kcal mole^{-1}.

The standard heat of formation of gaseous AuSi is obtained from the selected value for its dissociation energy and the heats of sublimation of the elements[10], (in kcal mole^{-1}): $\Delta H_{v,o}$(Au)$_f = 87.96 \pm 0.3$; $\Delta H_{v,st}$(Au) $= 88.0 \pm 0.3$; $\Delta H_{v,o}$(Si) $= 107.86 \pm 1.0$ and $\Delta H_{v,st}$(Si) $= 108.9 \pm 1.0$. It leads to $\Delta H_{f,o}$[AuSi(g)] $= 518.3 \pm$

TABLE 6

SELECTED DISSOCIATION ENERGY OF AuSi

Gas phase reaction		D_0^0 (AuSi) kJ mole^{-1}
AlAu + Si = AuSi + Al	(3rd Law)	295.9 ± 2.3[a]
	(3rd Law)	306.9[c,d]
Au$_2$ + Si = AuSi + Au	(3rd Law)	297.2 ± 3.1[a]
	(3rd Law)	306.2 ± 7[b]
	(2nd Law)	299.2 ± 12[b]
	(3rd Law)	309.2 ± 3.0[c]
AuSi = Au + Si	(3rd Law)	300.2 ± 3.7[a]
	(2nd Law)	297.3 ± 12 2[a]
	Selected value:	301.0 ± 6.0

[a] Present work.
[b] Ref. 5.
[c] Ref. 6.
[d] A weight of one-third has been given to this value.

TABLE 7

ION INTENSITIES OF PARENT IONS ABOVE THE CONDENSED SYSTEM Au–Si

Set No.	Temp. (K)	Ion intensities in A				
		I (Au$^+$)	I (Si$^+$)	I (AuSi$^+$)	I (Au$_2$Si$^+$)	I (AuSi$_2^+$)
1	1636	7.18 × 10^{-10}	1.59 × 10^{-11}	3.15 × 10^{-12}		
2	1660	1.74 × 10^{-9}	4.60 × 10^{-10}	7.35 × 10^{-12}		
3	1637	1.16 × 10^{-9}	1.47 × 10^{-11}	4.05 × 10^{-12}	1.62 × 10^{-13}	
4	1751	5.25 × 10^{-9}	2.26 × 10^{-10}	6.60 × 10^{-11}	1.475 × 10^{-12}	1.80 × 10^{-13}
5	1818	4.90 × 10^{-9}	2.62 × 10^{-10}	5.90 × 10^{-11}	1.12 × 10^{-12}	1.67 × 10^{-13}

6 kJ mole^{-1} or 124.8 ± 1.4 kcal mole^{-1}; $\Delta H_{f,298}$ [AuSi(g)] = 518.6 ± 6 kJ mole^{-1} or 123.9 ± 1.4 kcal mole^{-1}.

Atomization energies of Au$_2$Si and AuSi$_2$

Table 7 shows various ion intensities obtained in the run using an Au–Si alloy. For an evaluation of the free energy functions for the triatomic species the following points have been taken into consideration.

In accordance with the report by Houdart and Schamps[7] and Barrow et al.[15], the internuclear distance and vibrational frequency for AuSi were respectively obtained as r_e = 2.51 Å and ω_e = 391 cm^{-1} (corresponding to a stretching force constant of 2.23 mdyne-Å). An electronic contribution: A $^2\Sigma^+$, 13743.3 cm^{-1}; X_2 $^2\Pi_{3/2}$, 1072.0 cm^{-1}; X_1 $^2\Pi_{1/2}$, 0 cm^{-1}, was used.

In an analogy with the spectroscopically observed SiH_2[16] molecule, the Au_2Si molecule is assumed to be symmetric and bent, having the configuration C_{2v}. The measured bond angle of 105° for the molecule $SiCl_2$[17] is assumed to characterize the Au_2Si molecule as well. The above listed force constant of 2.23 mdyne-Å for the AuSi molecule plus the bending force constant 1.40 mdyne-Å and the electronic ground state $^2\Pi$ have been used to calculate the free energy functions of Au_2Si. Using the same parameters the thermal functions for the linear structure have also been evaluated.

Hydrogen and gold have similar electronegativities ($\chi_H = 2.1$ and $\chi_{Au} = 2.4$) if adjusted to correspond to the same valence state[18]. Additionally the bond dissociation energies of the diatomic molecules SiH and AuSi are similar, $[D_0^0(Si-H) = 295.4$ kJ mole^{-1}[2] and $D_0^0(AuSi) = 301.0$ kJ mole^{-1} (present work)]. These facts suggest monovalency of gold and hence an asymmetric configuration has been ascribed to $AuSi_2$.

For calculation of the thermal functions the same equilibrium distance r_e and stretching force constant k for AuSi are used. As for the Si_2 molecule[2], the Si–Si

TABLE 8

ESTIMATED VIBRATIONAL FREQUENCIES (IN CM^{-1}) OF THE GASEOUS MOLECULES Au₂Si AND AuSi₂

Molecule	ω_1	ω_2	ω_3
Au₂Si (L)	535	289 (d.d.)	138
(B)	445	90	374
AuSi₂ (L)	586	252 (d.d.)	256
(B)	520	155	399

TABLE 9

FREE ENERGY FUNCTIONS, $- (G_T^0 - H_T^0)/T$, IN J K^{-1} MOLE^{-1} AND HEAT CONTENT FUNCTIONS, $(H_T - H_0^0)$, IN kJ MOLE^{-1} FOR THE GASEOUS MOLECULES AuSi, Au₂Si AND AuSi₂

Molecule and structure		Temperature (K)						
		298	1200	1400	1600	1800	2000	2200
AuSi	FEF	224.8	274.1	279.9	285.1	289.6	293.6	297.2
	HCF	9.586	45.52	53.39	61.21	68.95	76.65	84.35
Au₂Si	FEF	267.9	340.4	349.3	357.0	363.9	370.1	375.8
Linear	HCF	13.58	68.45	80.32	93.26	105.7	118.1	130.6
Bent	FEF	295.1	365.0	373.42	380.7	387.2	393.1	398.4
	HCF	13.48	64.81	76.40	87.99	99.58	111.2	122.8
AuSi₂	FEF	252.7	323.2	331.9	339.6	346.4	352.5	358.2
Linear	HCF	12.93	67.45	79.83	92.22	104.6	117.1	129.5
Bent	FEF	278.8	347.0	355.3	362.5	368.9	374.7	380.0
	HCF	12.95	63.93	75.52	87.11	98.70	110.3	121.9

TABLE 10

THIRD-LAW ENTHALPIES FOR THE TRIATOMIC MOLECULES $Au_2Si(g)$ AND $AuSi_2(g)$

Reaction	$T(K)$	$log\ K_p$	$-\Delta[(G_T - H_0^0)/T]$ (J K^{-1} mole^{-1})		ΔH_0^0 (kJ mole^{-1})	
			Linear	Bent	Linear	Bent
$Au_2Si(g) + Si(g)$	1636	0.74	31.3	7.69	27.9	−10.7
= 2AuSi(g)	1751	1.12	31.1	7.66	17.0	−24.0
	1818	1.07	30.9	7.64	19.1	−23.3
				Average	21.3 ± 5.8	−19.3 ± 7.5
$AuSi_2(g) + Au(g)$	1751	0.70	35.8	13.2	39.2	−0.38
= 2AuSi(g)	1818	0.68	35.7	13.2	41.4	0.54
				Average	40.3 ± 1.6	0.08 ± 0.7

bond has been assumed to have $r_e = 2.34$ Å and a stretching force constant $= 2.10$ mdyne-Å. A bending force constant 1.27 mdyne-Å and ground electronic state $^2\Pi$ are assigned to $AuSi_2$.

Table 8 shows the calculated vibrational frequencies for molecules Au_2Si and $AuSi_2$. In these calculations, a method of normal coordinate analysis[19] was used.

The free energy functions of AuSi, Au_2Si and Si_2Au are shown in Table 9. For an evaluation of the atomization energies for the triatomic species, the following pressure independent gas phase reactions were considered.

$$Au_2Si + Si\ = 2AuSi \qquad\qquad (E)$$
$$AuSi_2 + Au = 2AuSi \qquad\qquad (F)$$

The third law enthalpies of these reactions are shown in Table 10. The values are 21.3 ± 5.8 and 40.3 ± 1.6 kJ mole^{-1} assuming linear structure and −19.3 ± 7.5 and 0.08 ± 0.7 kJ mole^{-1} for nonlinear structures, respectively, for reactions E and F.

Incorporation of the dissociation energy of AuSi(g) leads to the atomization energies of $Au_2Si(g)$ $\Delta H_{a,o} = 623.3 ± 15$ kJ mole^{-1} and 582.7 ± 15 kJ mole^{-1} for linear and bent structures, respectively. The evaluated atomization energies for the molecule $AuSi_2(g)$ for linear and bent structures $\Delta H_{a,o}$ are 642.3 ± 15 and 602.1 ± 15 kJ mole^{-1}, respectively. In analogy with the molecules Au_2Ge and $AuGe_2$[20] we give preference to the bent structures.

Using the heat of sublimation for the gaseous atoms Au (368.2 ± 1.3 kJ mole^{-1}) and Si (455.6 ± 4.2 kJ mole^{-1})[10] heats of formation at standard temperature are calculated from the above atomization energies. The calculated heats of formation $\Delta H_{f,298}$ for the linear and bent structuress of the gaseous molecule Au_2Si are respectively 558.2 and 602.9 kJ mole^{-1} and for the linear and bent structures of the molecules $AuSi_2$ are 629.0 and 668.9 kJ mole^{-1}, respectively.

TABLE 11

RATIOS OF THE ATOMIZATION ENERGIES OF $MAu_{2(g)}$, $M_2Au_{(g)}$ AND $M_2Au_{2(g)}$ RELATIVE TO THOSE OF $MAu_{(g)}$

M	Atomization energies $\Delta H_{a,0}^0$ (kJ mole^{-1})				Ratios of atomization energies		
	$MAu_{(g)}$	$MAu_{2(g)}$	$M_2Au_{(g)}$	$M_2Au_{2(g)}$	$MAu_{2(g)}/$ $MAu_{(g)}$	$M_2Au_{(g)}/$ $MAu_{(g)}$	$M_2Au_{2(g)}/$ $MAu_{(g)}$
Si[b]	301 ± 6	583 ± 15	602 ± 15	1035 ± 27[a]	1.94	2.00	3.44
Ge[c]	273 ± 5	537 ± 12	533 ± 8	929 ± 14	1.96	1.95	3.40
Sn[d]	251 ± 8	542 ± 18	486 ± 18	871 ± 25	2.16	1.94	3.47

[a] Estimated atomization energy.
[b] Present work.
[c] Ref. 20.
[d] Ref. 21.

CONCLUSION

The data on the molecules involving Au and Si may be compared with those for other group IVB–gold molecules. Table 11 shows the ratios of the experimental atomization energies of the various group IVB–gold compounds to the dissociation energies of the diatomic molecules. A trend toward constancy in the ratios is evident. Although the elements considered include silicon, a nonmetal and tin, a typical metal, the approximate consistency in the ratios indicates similarity in the nature of bonding in these molecules. On the basis of the dimer to monomer atomization energy ratio equal to 3.44, the value for the molecule Au_2Si_2 has been estimated (see Table 11). Lead–gold molecules are expected to show similar characteristics.

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REFERENCES

1 K. A. Gingerich, J. Cryst. Growth, 9 (1971) 31.
2 B. Rosen (Ed.), Spectroscopic Data Relative to Diatomic Molecules, Pergamon Press, Oxford, 1970.
3 E. Chattilon, M. Allibert and A. Pattoret, C. R. Acad. Sci., Ser. C, 280 (1975) 1505.
4 H. R. Ihle and C. H. Wu, private communication, 1977.
5 A. Vander Auwera-Mahieu, R. Peeters, N. S. McIntyre and J. Drowart, Trans. Faraday Soc., 66 (1970) 809.
6 K. A. Gingerich, J. Chem. Phys., 50 (1969) 5426.
7 R. Houdart and J. Schamps, J. Phys. B, 6 (1973) 2478.
8 K. A. Gingerich, J. Chem. Phys., 49 (1968) 14.

9   R. T. Grimley, in J. L. Margrave (Ed.), *Characterization of High Temperature Vapors*, Wiley, New York, 1967, pp. 195–273.

10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of Thermodynamic Properties of Elements*, Am. Soc. Met. Metals Park, Ohio, 1973.

11 J. Kordis, K. A. Gingerich and R. J. Seyse, *J. Chem. Phys.*, 61 (1974) 5114.

12 J. B. Mann, in K. Ogata and T. Hayakawa (Eds.), *Recent Developments in Mass Spectrometry*, University Tokyo Press, 1970, pp. 814–819.

13 J. Drowart and P. Goldfinger, *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 581.

14 K. A. Gingerich and G. D. Blue, *J. Chem. Phys.*, 59 (1973) 185.

15 R. F. Barrow, W. J. M. Gissane and D. N. Travis, *Nature (London)*, 201 (1964) 603.

16 D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 52 (1970) 2594.

17 G. Maas, R. H. Hauge and J. L. Margrave, *Z. Anorg. Allg. Chem.*, 392 (1972) 295.

18 W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, 24 (1956) 439.

19 J. H. Schachtschneider and R. G. Snyder, *Spectrochimi Acta*, 19 (1963) 117.

20 J. E. Kingcade, Jr., *M.Sc. Thesis*, Texas A & M University, 1978.

21 K. A. Gingerich, D. L. Cocke and U. V. Choudary, *Inorg. Chim. Acta*, 14 (1975) L47.