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Electronic structure of Ge_2 and Ge_2^- and thermodynamic properties of Ge_2 from all electron ab initio investigations and Knudsen effusion mass spectroscopic measurements

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Abstract

The low-lying states of the molecule Ge_2 and of the ion Ge_2^- have been investigated by all electron ab initio multi-configuration self-consistent field (CASSCF) and multi-reference configuration interaction (MRCI) calculations. The relativistic corrections for the Darwin contact term and for the mass–velocity term have been determined in perturbation calculations. Treatment of the spin-orbit coupling has been included. The ground state of Ge_2 is derived as $0^+({}^3\Sigma_g^-)$ with equilibrium distance 2.422 Å, and vibrational frequency 270 cm^{-1} . The spectroscopic constants of 15 excited states are presented. Thermal functions based on the theoretically determined molecular parameters were used to derive the thermodynamic properties of the Ge_2 molecule from new mass spectrometric equilibrium data. The literature value for the dissociation energy of Ge_2 has been re-evaluated. The recommended dissociation energy, $D_0^\circ(\text{Ge}_2)$, and enthalpy of formation, $\Delta_f H_{298.15}^\circ(\text{Ge}_2)$, in kJ mol^{-1} are 260.7 ± 6.8 and 484.8 ± 6.8 , respectively. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ge_2 ; Ge_2^- ; MRCI calculations; Electronic states; Mass spectroscopic measurements; Dissociation energy

1. Introduction

In previous all electron ab initio HF valence-CI calculations on the Ge_2 molecule [1,2], we

have described its electronic structure and bonding and have derived spectroscopic constants and relative electronic energies for several low-lying states. These results were used in the thermodynamic evaluation of the dissociation energy of the molecule from mass spectrometric equilibrium measurements [2]. Other authors have reported results of ab initio investigations using pseudo-potentials for Ge_2 [3–6]. All the theoretical investigations predict a ${}^3\Sigma_g^-$ ground state and a close lying ${}^3\Pi_u$ first excited state, but

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they differ somewhat in the excitation energy of the latter.

The first reported experimental spectroscopic investigation is the Raman and fluorescence study of Ge₂ in argon and krypton matrices by Froben and Schultze [7], yielding the ground state vibrational frequency as 274 cm⁻¹. Recently Li et al. [8] have reported magneto-infrared absorption spectra of Ge₂ isolated in neon and argon matrices. They determined the transition energy $^3\Pi_u \leftarrow ^3\Sigma_g^-$ as $T_e = 694$ cm⁻¹. Neumark and co-workers [9] have studied the zero electron kinetic energy (ZEKE) spectrum and the lower resolution photoelectron spectrum (PES) [10] of Ge₂⁻. They determined the term energies of the spin-orbit components of the $^3\Sigma_g^-$ ground state and of the low-lying $^3\Pi_u$ state, and also of the next higher lying states, $^1\Delta_g$, $^3\Sigma_g^+$, and $^1\Pi_u$ of Ge₂ [9].

In the present investigation we have performed complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MRCI) calculations including relativistic effects and spin-orbit coupling for Ge₂ and Ge₂⁻. In addition, we present new mass spectrometric equilibrium data for Ge₂ obtained over pure germanium in connection with the investigation of gaseous germanium carbides [11]. An improved value for the dissociation energy and heat of formation has been determined using the new thermal functions derived from the molecular parameters determined in the present investigation. We have also re-evaluated the literature mass spectrometric equilibrium data for gaseous Ge₂ employing the present thermal functions after correcting the reported partial pressures to be consistent with the assumptions used in the present work.

2. Theoretical investigations

The low-lying electronic states of the molecules Ge₂ and Ge₂⁻ have been investigated by carrying out all electron ab initio CASSCF and MRCI calculations. The relativistic effects on the low-lying states have been considered by performing perturbation calculations of the one electron Darwin contact term and also of the relativistic

mass velocity term. The effect of spin-orbit coupling has been taken into account by utilizing the perturbational Hamiltonian $H' = \sum \xi(r_i) \mathbf{L}_i \cdot \mathbf{s}_i$. The program system MOLCAS, version 3 [12] has been used for the ab initio calculations.

The wave functions have been expanded in basis sets consisting of contracted Gaussian type functions. Huzinaga's (14s, 11p, 5d) basis [13] has been used, but the exponents of the most diffuse s and p functions have been increased slightly; a diffuse s and a diffuse p function have been added. The exponents of the three most diffuse s functions in the final basis set are 0.3472, 0.1033, and 0.0369, and those of the most diffuse p functions are 0.3086, 0.1224, and 0.052. Furthermore, the basis set has been augmented with one d function with exponent 0.225347 and one f function with exponent 3.438. Using segmented contraction the primitive basis (15s, 12p, 6d, 1f) has been contracted to (9s, 7p, 3d, 1f) resulting in triple zeta representation of the valence orbitals, 4s, 4p, as well as of the 3d orbitals. The core orbitals, 1s, 2s, 3s, 2p, and 3p, are represented by double zeta functions.

In the CASSCF calculations the core orbitals, i.e. 1s, 2s, 3s, 2p, 3p, 3d of Ge, have been kept fully occupied, while the valence orbitals, 4s and 4p, have been included in the active space. The CASSCF calculations have been performed in the subgroup D_{2h} of the full symmetry group D_{∞h} of Ge₂ and Ge₂⁻. The MRCI calculations have been carried out by including all single and double excitations from all the configurations in the CASSCF calculations.

The spectroscopic constants for both molecules have been derived by solving the Schrödinger equation for the nuclear motion numerically.

2.1. The Ge₂ molecule

For the seven lowest-lying bound states of Ge₂ identified in our previous investigations [1,2] CASSCF calculations have been performed at the internuclear distances 4.0, 4.2, 4.4, 4.5, 4.6, 4.8, 5.0, 5.2, 5.4, 6.0, 7.0, and 12.0 a.u.

The numbers of configurations included in the CASSCF calculations for the triplet states, $^3\Sigma_g^-$ and $^3\Pi_u$, are 292 and 296, respectively. For the

singlet states, $^1\Delta_g$, $^1\Pi_u$, and $^1\Sigma_g^+$, 204, 216, and 264 configurations were included, and 88 configurations were included for the $^5\Pi_g$ state. The molec-

ular orbitals optimized in the CASSCF calculations have been utilized as the basis in MRCI calculations. The number of configurations

Table 1

Spectroscopic constants of the low-lying electronic states of the Ge_2 molecule as derived from the results of MRCI calculations including relativistic corrections

State	Equilibrium distance, r_e (Å)	Vibrational frequency, ω_e (cm^{-1})	Transition energy, T_e (cm^{-1})	Dissociation energy, D_e^a (eV)
$^3\Sigma_g^-$	2.422	271	0	2.39
$^3\Pi_u$	2.320	278	679	2.30
$^1\Delta_g$	2.467	249	3683	1.93
$^1\Sigma_g^+$	2.448	206	5168	1.75
$^1\Pi_u$	2.323	270	5383	1.72
$^5\Pi_g$	2.611	338	8842	1.29
$\Pi^1\Sigma_g^+$	2.344	408	9960	1.15

^a Derived as the difference between the total molecular energy at the equilibrium distance and the sum of the energy of two Ge atoms in their 3P ground term determined by the same method.

Table 2

The contributions of the major configurations to the MRCI wave functions describing the $^3\Sigma_g^-$ ground state and the excited states, $^3\Pi_u$, $^1\Delta_g$, $^1\Sigma_g^+$, $^1\Pi_u$, $^5\Pi_g$, and $\Pi^1\Sigma_g^+$ of the Ge_2 molecule as functions of the internuclear distance

State	Valence shell configuration						Contribution of valence shell configuration (%)								
	4s σ_g	4s σ_u	4p σ_g	4p π_u	4p π_g	4p σ_u	Internuclear distance (a.u.)								
							4.0	4.2	4.4	4.5	4.6	4.8	5.0	5.2	5.4
$^3\Sigma_g^-$	2	2	2	2	0	0	87	85	85	85	84	83	82	81	80
$^3\Pi_u$	2	2	1	3	0	0	83	82	81	81	80	79	77	75	73
$^1\Delta_g$	2	2	2	2	0	0	86	85	84	83	82	81	79	78	75
$^1\Sigma_g^+$	2	2	0	4	0	0	72	62	37	24	16	9	6	5	4
	2	2	2	2	0	0	6	17	43	57	64	69	71	70	69
$^1\Pi_u$	2	2	1	3	0	0	83	82	81	80	80	78	76	74	71
$^5\Pi_g$	2	2	1	2	1	0	88	87	87	87	87	87	87	86	86
$^1\Sigma_g^+$	2	2	0	4	0	0	5	14	38	49	56	60	60	58	54
	2	2	2	2	0	0	70	62	37	23	16	9	6	4	3

Table 3

Results of population analysis for the low-lying electronic states of Ge_2 based on the MRCI wave functions at 4.5 a.u. Also included are the number of d electrons on each Ge atom

State	Number of d electrons	Population								
		4s σ_g	4s σ_u	4p σ_g	4p σ_u	4p π_g	4p π_u	4s	4p σ	4p π
$^3\Sigma_g^-$	10.09	1.95	1.92	1.90	1.93	0.13	0.05	1.88	1.02	1.01
$^3\Pi_u$	10.08	1.95	1.90	1.00	2.78	0.22	0.04	1.83	0.61	1.48
$^1\Delta_g$	10.08	1.95	1.92	1.90	1.89	0.17	0.05	1.89	1.01	1.02
$^1\Sigma_g^+$	10.08	1.95	1.90	1.36	2.42	0.23	0.04	1.85	0.76	1.31
$^1\Pi_u$	10.08	1.95	1.90	0.99	2.79	0.22	0.05	1.83	0.61	1.48
$^5\Pi_g$	10.08	1.95	1.91	1.00	1.96	1.04	0.03	1.84	0.59	1.48
$\Pi^1\Sigma_g^+$	10.07	1.94	1.86	0.66	3.06	0.34	0.04	1.79	0.45	1.69

included in the final MRCI calculations amount to 1 325 804 for $^3\Sigma_g^-$, 1 341 432 for $^3\Pi_u$, 767 572 for $^1\Delta_g$, 782 096 for $^1\Pi_u$, 800 000 for $^1\Sigma_g^+$, and to 630 060 for $^5\Pi_g$.

The spectroscopic constants derived on the basis of the MRCI calculations are reported in Table 1 together with the dissociation energies. Table 2 shows the contributions of the major configurations for the low-lying electronic states as functions of the internuclear distance and Table 3 shows results of population analysis for the low-lying states based on the MRCI wave functions. Fig. 1 shows the potential energy curves

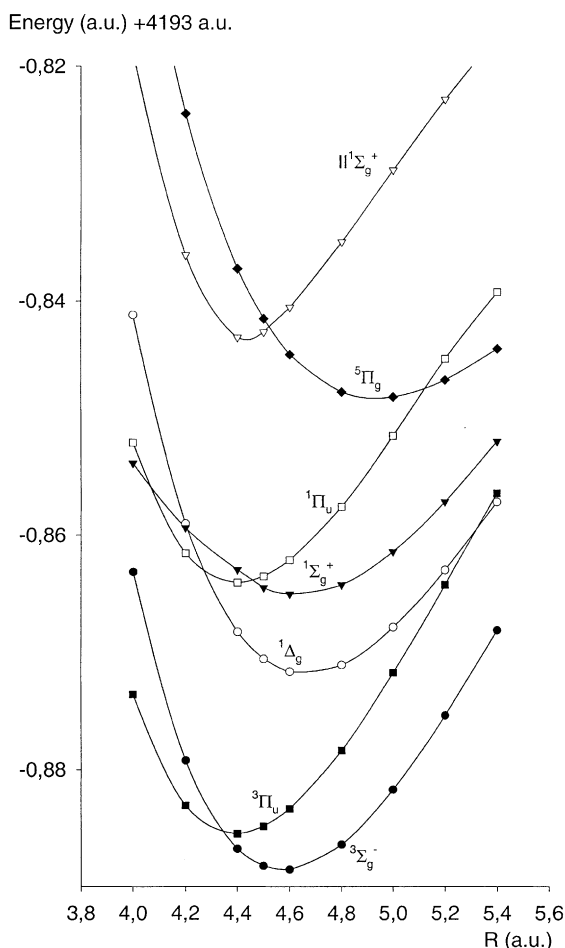


Fig. 1. Potential energy curves for the seven lowest-lying states of Ge_2 as derived in MRCI calculations including relativistic corrections.

for the seven lowest-lying states as derived in the MRCI calculations including the relativistic corrections.

In both, the CASSCF and the MRCI calculations, the electronic ground state is derived as $^3\Sigma_g^-$ with the major configuration $(4s\sigma_g)^2(4s\sigma_u)^2(4p\sigma_g)^2(4p\pi_u)^2$. This configuration is also the major configuration of the $^1\Delta_g$ state and of the lowest-lying $^1\Sigma_g^+$ state at internuclear distances larger than 4.4 a.u. The two low-lying $^1\Sigma_g^+$ states are mixtures of the configurations $(4s\sigma_g)^2(4s\sigma_u)^2(4p\sigma_g)^2(4p\pi_u)^2$ and $(4s\sigma_g)^2(4s\sigma_u)^2(4p\pi_u)^4$, and a crossover of configurations occurs close to 4.4 a.u. The major configuration of both the states, $^3\Pi_u$ and $^1\Pi_u$, is $(4s\sigma_g)^2(4s\sigma_u)^2(4p\sigma_g)^1(4p\pi_u)^3$, and of $^5\Pi_g(4s\sigma_g)^2(4s\sigma_u)^2(4p\sigma_g)^1(4p\pi_u)^2(4p\pi_g)^1$. Thus, the states $^3\Sigma_g^-$ and $^1\Delta_g$ represent different space and spin couplings within the $(4p\pi_u)^2$ configuration. Likewise, the states $^3\Pi_u$ and $^1\Pi_u$ are singlet and triplet couplings within the configuration $(4p\sigma_g)^1(4p\pi_u)^3$. These findings are consistent with our previous work [1,2], and also with the results of other workers [3–6].

In both, the CASSCF and the MRCI calculations, the effect of the relativistic corrections are modest. However, relative to the CASSCF calculations the energy separation between the $^3\Sigma_g^-$ ground state and the first excited $^3\Pi_u$ state is increased from 125 to 679 cm^{-1} in the MRCI calculations. The latter value is in very good agreement with the experimental value of 694 cm^{-1} by Li et al. [8].

The equilibrium distance for the $^3\Sigma_g^-$ ground state is determined as 2.422 Å and the vibrational frequency as 271 cm^{-1} . The latter value agrees well with the experimentally determined values of 274 or 277 cm^{-1} [7].

The spin-orbit coupling has been considered by performing perturbation calculations using the Hamiltonian $H' = \sum \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i$ and the spin-orbit coupling constant ξ as 984 cm^{-1} derived from Moore's tables [14]. Fig. 2 shows the potential energy curves for the low-lying spin-orbit coupled states. Table 4 displays the spectroscopic constants obtained for the spin-orbit coupled states. The sequence of the low-lying states is identical to that measured by Arnold et al. [9], and there is also

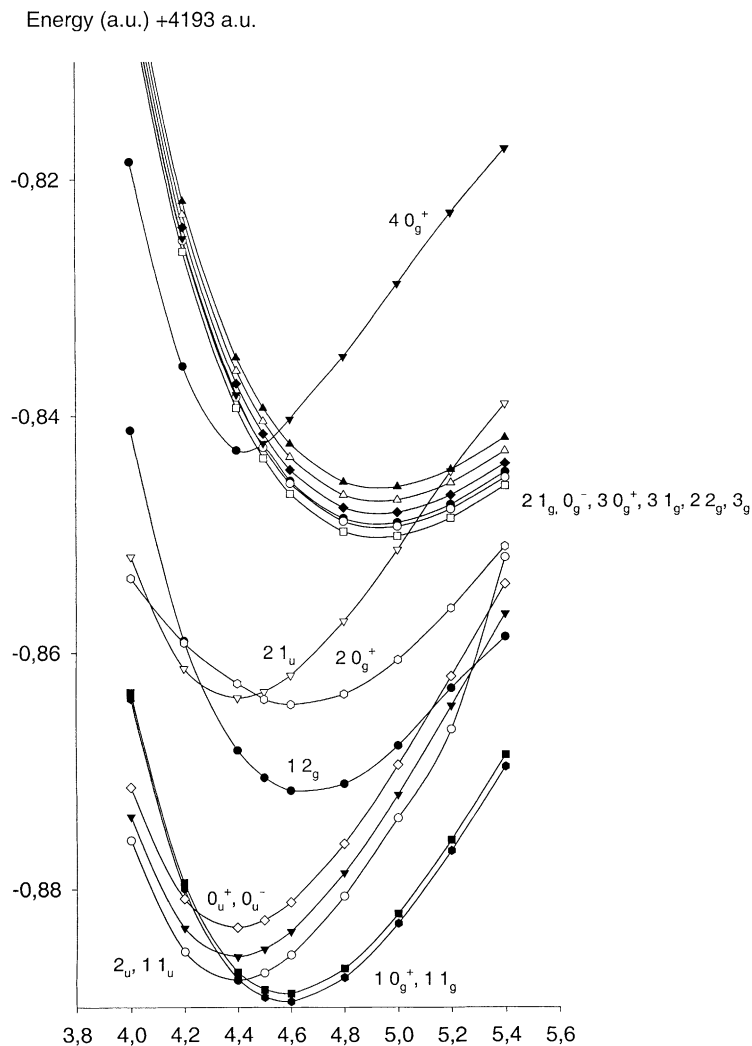


Fig. 2. Potential energy curves for the low-lying spin-orbit coupled states of Ge_2 .

good agreement between the calculated and the measured transition energies. The vibrational frequency for $1_g(^3\Sigma_g^-)$ is determined as 270 cm^{-1} by us and as $286 \pm 5\text{ cm}^{-1}$ by Arnold et al. [9]. The vibrational frequencies of the higher lying states, $0_u^-(^3\Pi_u)$, $^1\Delta_g$, and $^1\Pi_u$ as determined by us are lower than those of [9] by 30, 28, and 33 cm^{-1} , respectively [9]. The vibrational frequency of 206 cm^{-1} derived for the lowest-lying $^1\Sigma_g^+$ state is within the experimental error limit of $204 \pm 7\text{ cm}^{-1}$ [9].

The dissociation energy D_e is derived as 2.29 eV, and D_0 as 2.27 eV. This is 84% of the experimental value derived in the present work.

2.2. The Ge_2^- ion

From [9,10] it is known that the Ge_2^- molecule has two low-lying electronic states, $^2\Pi_u$ and $^2\Sigma_g^+$. CASSCF calculations have been performed for these states at the internuclear distances 4.0, 4.2, 4.4, 4.6, 4.8, and 5.0 a.u.

Table 4

Spectroscopic constants of the low-lying electronic states of the Ge_2 molecule as derived from the results of MRCI calculations including relativistic corrections and spin-orbit coupling

State	Equilibrium distance, r_e (Å)	Vibrational frequency, ω_e (cm^{-1})	Transition energy, T_e (cm^{-1})	Dissociation energy ^a , D_e (eV)
$0_g^+(^3\Sigma_g^-)$	2.424	270	0	2.29
$1_g(^3\Sigma_g^-)$	2.423	270	150	2.27
$2_u(^3\Pi_u)$	2.320	278	397	2.24
$1_u(^3\Pi_u)$	2.320	278	838	2.19
$0_u^+, 0_u^-(^3\Pi_u)$	2.320	278	1381	2.12
$2_g(^1\Delta_g)$	2.466	248	3894	1.81
$0_g^+(^1\Sigma_g^+)$	2.443	206	5522	1.61
$1_u(^1\Pi_u)$	2.323	270	5644	1.59
$1_g(^5\Pi_g)$	2.609	331	8625	1.22
$0_g^-(^5\Pi_g)$	2.611	338	8806	1.20
$0_g^+(^5\Pi_g)$	2.614	330	8880	1.19
$1_g(^5\Pi_g)$	2.611	337	9064	1.17
$2_g(^5\Pi_g)$	2.611	338	9298	1.14
$3_g(^5\Pi_g)$	2.611	338	9544	1.11
$0_g^+(^1\Sigma_g^+)$	2.387	710	10361	1.01

^a Derived as the difference between the total molecular energy at the equilibrium distance and the sum of energy of the separated atoms including spin-orbit coupling.

The number of configurations included in the CASSCF calculations was 294 for the $^2\Pi_u$ state and 308 for the $^2\Sigma_g^+$ state. The number of configurations included in the final MRCI calculations amounts to 1718078 for $^2\Pi_u$, and to 1772976 for $^2\Sigma_g^+$.

Table 5 shows the spectroscopic constants as derived from the MRCI calculations excluding and including relativistic corrections. Also included are the spectroscopic constants of the spin-orbit coupled states. Table 6 shows the contributions of the major configurations for the low-lying electronic states as functions of the internuclear distance as

derived from the MRCI wave functions. Table 7 shows results of population analysis for the low-lying states based on the MRCI wave functions. Figs. 3 and 4 show potential energy curves for Ge_2^- . Fig. 3 shows the potential energy curves as derived in the MRCI calculations including the relativistic corrections, and Fig. 4 shows the potential energy curves for the spin-orbit coupled states.

In both, the CASSCF and the MRCI calculations, the electronic ground state is derived as $^2\Sigma_g^+$ with the major configuration $(4s\sigma_g)^2(4s\sigma_u)^2(4p\sigma_g)^1(4p\pi_u)^4$. The major configuration of the

Table 5

Spectroscopic constants of the low-lying electronic states of the Ge_2^- molecule as derived from the results of MRCI calculations

State	Method:	Without relativistic corrections				With relativistic corrections			
		Equilibrium distance, r_e (Å)	Vibrational frequency, ω_e (cm^{-1})	Transition energy, T_e (cm^{-1})	Electron affinity, E_e^a (eV)	Equilibrium distance, r_e (Å)	Vibrational frequency, ω_e (cm^{-1})	Transition energy, T_e (cm^{-1})	Electron affinity, E_e^a (eV)
$^2\Sigma_g^+$		2.275	328	0	1.67	2.267	329	0	1.61
$^2\Pi_u$		2.354	278	86		2.346	275	68	
$^2\Pi_{u3/2}$		2.354	278	−406		2.346	275	−423	1.64
$^2\Pi_{u1/2}$		2.354	278	578		2.346	275	560	

^a Derived as the difference between the total energy at the equilibrium distance between the Ge_2^- ion and the Ge_2 molecule determined by the same method.

Table 6

The contributions of the major configurations to the MRCI wave functions describing the two lowest-lying states, $^2\Sigma_g^+$ and $^2\Pi_u$, of the Ge_2^- ion as functions of the internuclear distance

State	Valence shell configuration						Contribution of valence shell configuration (%)					
	4s σ_g	4s σ_u	4p σ_g	4p π_u	4p π_g	4p σ_u	Internuclear distance (a.u.)					
							4.0	4.2	4.4	4.6	4.8	5.0
$^2\Sigma_g^+$	2	2	1	4	0	0	80	79	77	75	73	70
$^2\Pi_u$	2	2	2	3	0	0	84	83	82	80	79	77

Table 7

Results of population analysis for the low-lying electronic states of Ge_2^- based on the MRCI wave functions at 4.4 a.u. Also included are the number of d electrons on each Ge atom

State	Number of d electrons	Population								
		4s σ_g	4s σ_u	4p σ_g	4p π_u	4p π_g	4p σ_u	4s	4p σ	4p π
$^2\Sigma_g^+$	10.07	1.96	1.91	1.00	3.67	0.29	0.04	1.82	0.64	1.97
$^2\Pi_u$	10.08	1.96	1.93	1.91	2.83	0.20	0.05	1.89	1.03	1.50

$^2\Pi_u$ state is $(4s\sigma_g)^2(4s\sigma_u)^2(4p\sigma_g)^2(4p\pi_u)^3$. The transition energy is derived as 798 cm^{-1} in the CASSCF calculations, but this is reduced to 86 cm^{-1} in the MRCI calculations without relativistic corrections. Taking into account the relativistic corrections the corresponding energy differences are 784 and 68 cm^{-1} , respectively. Both states, $^2\Sigma_g^+$ and $^2\Pi_u$, can be considered as derived from the $^3\Pi_u$ state of the Ge_2 molecule by addition of one electron. The $^2\Sigma_g^+$ state results when an electron is added to the $4p\pi_u$ orbital, and the $^2\Pi_u$ state arises by adding an electron to the $4p\sigma_g$ orbital.

Experimentally the ground state has been determined as $^2\Pi_{u3/2}$ [9,10]. Our results, however, are consistent with the results of the experimental work, since the spin-orbit coupling splits the $^2\Pi_u$ state into $^2\Pi_{u3/2}$ and $^2\Pi_{u1/2}$. Using the spin-orbit coupling constant, $\xi = 984\text{ cm}^{-1}$, for Ge as deduced from Moore's tables [14], the energy of the $^2\Pi_{u3/2}$ state will be lower than that of $^2\Sigma_g^+$ by 423 cm^{-1} . A ξ value of 694 cm^{-1} reproduces the experimental splitting of 279 cm^{-1} between the states $^2\Pi_{u3/2}$ and $^2\Sigma_g^+$. The vibrational frequency for the $^2\Sigma_g^+$ state is derived as 329 cm^{-1} and that of $^2\Pi_u$ as 275 cm^{-1} . While the value for the $^2\Sigma_g^+$ state is within the error limits of the experimental value, $326 \pm 10\text{ cm}^{-1}$, the value for the $^2\Pi_u$ state, 275

cm^{-1} , is lower than the experimental value of $309 \pm 5\text{ cm}^{-1}$ [9,10]. The electron affinity, 1.61 eV , derived as the energy difference between the $^2\Sigma_g^+$ state of Ge_2^- and the $^3\Sigma_g^-$ of Ge_2 at the equilibrium distances, or as 1.64 eV derived between the $^2\Pi_{u3/2}$ state of Ge_2^- and the 0_g^+ state of Ge_2 . These values are less than the experimental value by 0.42 and 0.39 eV , respectively [9]. This discrepancy is presumably connected with the basis set, since the same basis set is used to investigate both Ge_2 and Ge_2^- .

3. Mass spectroscopic measurements

3.1. Experimental procedure

A Nuclide corporation magnetic deflection single focusing Knudsen cell mass spectrometer was used in this investigation. The specific instrument [15] and experimental procedures employed have been described elsewhere [16]. The experimental equilibrium data for Ge_2^+ and Ge^+ evaluated in the present investigation have been obtained simultaneously with the germanium carbide clusters measured in series 1 and 2 reported previously [11]. The electron impact energy scale was calibrated with reference to the known first

Energy (a.u.) + 4193 a.u.

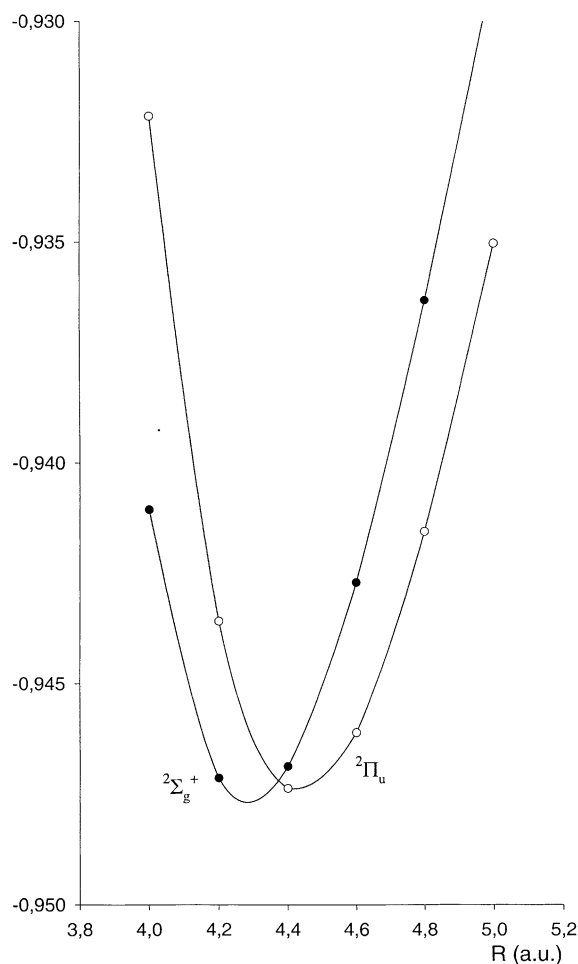


Fig. 3. Potential energy curves for the two low-lying states of Ge_2^- as derived in MRCI calculations including relativistic corrections.

ionization potential of Ge (7.88 V) and/or Ag (7.57 V) [14]. The appearance potential of Ge_2 was found to be 7.7 ± 0.5 eV.

In the present investigation the condensed germanium was at unit activity and the partial pressure p_{Ge}° can be calculated from the known enthalpy of formation of $\text{Ge}(\text{g})$ [17], $\Delta_f H_0^\circ = 371.7 \pm 2.1$ kJ mol $^{-1}$ using the relation

$$p_{\text{Ge}}^\circ = \exp\left\{-[\Delta_f H_0^\circ(\text{Ge})/RT - T\Delta(G_T^\circ - H_0^\circ/T)/RT]\right\}.$$

Energy (a.u.) + 4193 a.u.

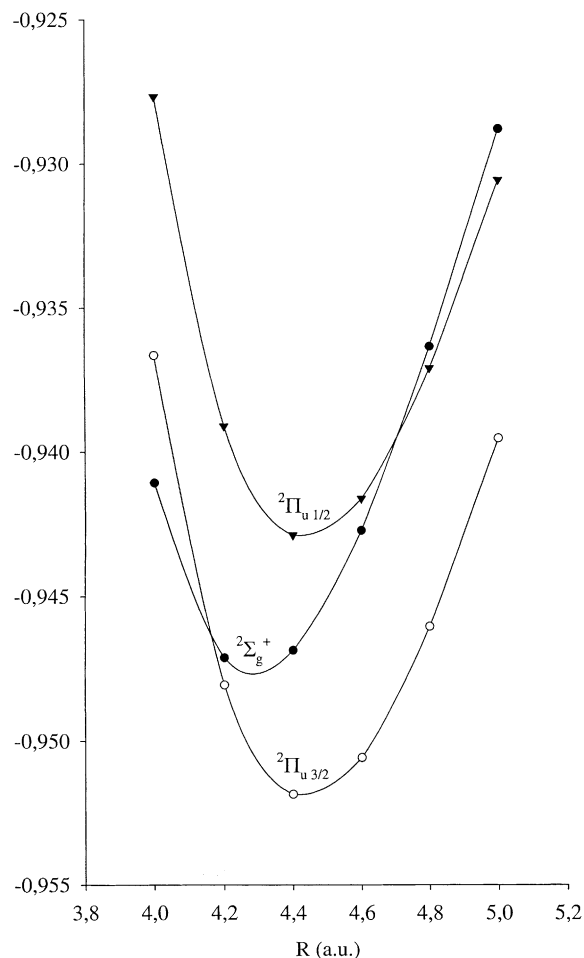


Fig. 4. Potential energy curves for the low-lying spin-orbit coupled states of Ge_2^- .

The pressure calibration constant, $k_{\text{Ge}} = p_{\text{Ge}}^\circ / (I_{\text{Ge}^+}^\circ T)$, was evaluated for each set of measurements. Thermal functions for $\text{Ge}(\text{l})$ and $\text{Ge}(\text{g})$ were taken from Gurvich et al. [18]. The calibration constant for Ge_2 was calculated from k_{Ge} employing the relation

$$k_i = k_{\text{ref}}(\sigma\gamma n)_{\text{ref}}/(\sigma\gamma n)_i, \\ \text{ref} = \text{Ag, Au or Ge}, \quad i = \text{Ge or Ge}_2.$$

The isotopic abundance of Ge, $n(^{74}\text{Ge}) = 0.366$, was taken from De Bievre and Barnes [19], and that of Ge_2 was calculated from that of Ge as

Table 8

Experimental and estimated parameters used in deriving the pressure calibration constants employed in the present study and those available in the literature

Reference	k_i derived based on	E (eV)	σ_{M2}/σ_M , $M = \text{Ag or Au}$	i	σ_i^a ($\times 10^{-16} \text{ cm}^2$)	$\gamma_i/\gamma_{\text{Ge}}$	k_i^b (atm $\text{A}^{-1} \text{ K}^{-1}$)
Series 1	$\text{Ge(l)} = \text{Ge(g)}$	14		Ge	4.46	1.00	13.6 ± 1.1
				Ge_2	6.69	1.00	13.9
Series 2	$\text{Ge(l)} = \text{Ge(g)}$	11		Ge	2.34	1.00	$(6.1 \pm 0.1) \times 10^{-2}$
				Ge_2	3.51	1.00	6.3×10^{-2}
[26], Au–Ge–Cu	$\text{Au}_2(\text{g}) = 2\text{Au(g)}$	20	1.5	Au	4.66	0.73 ^c	$(3.7 \pm 0.7) \times 10^{-1}$
				Ge	6.40	1.00	2.0×10^{-1}
				Ge_2	9.60	1.00	1.3×10^{-1}
				Ag	4.39	0.95 ^c	$(7.2 \pm 0.7) \times 10^{-2}$
[2], Sc–Ge+Ag	$\text{Ag}_2(\text{g}) = 2\text{Ag(g)}$	19	2.1	Ge	6.27	1.00	4.8×10^{-2}
				Ge_2	9.41	1.00	3.2×10^{-2}
				Ag	4.50	0.94 ^c	$(3.1 \pm 0.5) \times 10^{-2}$
				Ge	6.40	1.00	2.0×10^{-2}
[2], Pd–Ge+Ag	$\text{Ag}_2(\text{g}) = 2\text{Ag(g)}$	20	2.0	Ge_2	9.60	1.00	1.4×10^{-2}
				Ag	4.50	0.94 ^c	$(4.3 \pm 1.3) \times 10^{-2}$
				Ge	6.40	1.00	2.8×10^{-2}
				Ge_2	9.60	1.00	1.9×10^{-2}

^a σ_{Ag} and σ_{Ge} are taken from [32]. σ_{Au} from [31] and $\sigma_{\text{Ge}_2} = 1.5\sigma_{\text{Ge}}$.

^b The error is the standard deviation of the mean.

^c The experimentally determined multiplier gain [26,34].

$n(^{146}\text{Ge}_2) = 0.238$. The ionization cross-section σ of Ge_2 was taken to be 1.5 times that of Ge. The multiplier gain γ of Ge_2 was taken to be the same as that of Ge assuming cancellation of the ‘mass’ and ‘molecular’ effects [16,20]. Table 8 gives the calibration constants derived for series 1 and 2.

3.2. Experimental results

The enthalpy of the dissociation reaction

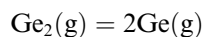


Table 9

Gibbs energy functions, $(-G_T^\circ - H_0^\circ)/T$, in $\text{J K}^{-1} \text{ mol}^{-1}$, and heat content functions, $H_T^\circ - H_0^\circ$, in kJ mol^{-1} , for the molecule Ge_2

T (K)	$H_T^\circ - H_0^\circ$	$-(G_T^\circ - H_0^\circ)/T$
298.15	11.42	219.29
1200	48.06	274.40
1400	56.06	280.57
1600	64.07	285.92
1800	72.13	290.63
2000	80.22	294.86
2200	88.37	298.68
2400	96.55	302.18

was evaluated by both the second-law and third-law methods using the standard relationships:

$$\ln(K_p) = -(\Delta H_T^\circ/RT) + (\Delta S_T^\circ/R)$$

and

$$\Delta H_0^\circ = -T\{R \ln K_p + \Delta(G_T^\circ - H_0^\circ/T)\}.$$

For $\text{Ge}_2(\text{g})$ the thermal functions were calculated using the harmonic oscillator, rigid rotator approximation and the molecular parameters derived in the MRCI calculations, including relativistic corrections and spin-orbit coupling, Table 4. The values obtained are listed in Table 9. The resulting second- and third-law enthalpies for the dissociation reaction from the measurements in series 1 and 2 are given in Table 10. The agreement between the second- and third-law enthalpies is good for both sets of measurements. The average second-law enthalpy of formation of atomic germanium, $\Delta_f H_{298.15}^\circ[\text{Ge(g)}]$ of series 1 ($377.5 \pm 7.8 \text{ kJ mol}^{-1}$) and series 2 ($370.9 \pm 6.8 \text{ kJ mol}^{-1}$) is $374.2 \pm 3.3 \text{ kJ mol}^{-1}$, the error being the standard deviation of the mean. This value is in good agreement with that recommended by Hultgren et al. [17], $\Delta_f H_{298.15}^\circ[\text{Ge(g)}] = 374.5 \pm 2.1 \text{ kJ mol}^{-1}$,

and thus supports our use of Hultgren's value of enthalpy of formation of Ge(g).

The selected ΔH_0° value for the dissociation reaction $\text{Ge}_2(\text{g}) = 2\text{Ge}(\text{g})$ given in Table 10 for series 1 and 2 is the weighted average of the second- and third-law values (weight of 2 for the third-law value and 1 for the second-law value). The recommended dissociation energy obtained in the present investigation, $D_0^\circ = 263.2 \pm 6.8 \text{ kJ mol}^{-1}$, based on these two series is the weighted average of the selected values. Here the weight for each selected value was taken proportional to the square root of number of data. The error given is the overall uncertainty estimated as in [21].

3.3. Re-evaluation of literature data

We have also re-evaluated the available literature equilibrium data [2,22–29] for the reaction $\text{Ge}_2(\text{g}) = 2\text{Ge}(\text{g})$ and have combined the results with those of the present investigation to obtain an assessed value of the dissociation energy of Ge_2 . In order to make a meaningful comparison with the results obtained in the present work, we have in this re-evaluation: (a) adopted the thermal functions used in the present work (b) derived the

pressure calibration constant by taking the reference partial pressure of Ge adopted in the present work, and (c) used a consistent set of ionization cross-sections and multiplier gains. The re-evaluated data have been included in Table 10. The evaporation coefficient was assumed to be unity in the re-evaluation of Honig's [22] and of Drowart and Honig's [23] data.

In the re-evaluation of the data from Kingcade et al. [2,26] the pressure calibration constants were derived based on the experimental cross-sections for Ag and Ge by Freund et al. [30] instead of those from Mann [31]. For Ag and Ag_2 the relative experimental ratio of ionization cross-sections as a function of electron energy [32] was employed. For the silver dimer the value of $D_0^\circ = 158.0 \pm 3.4 \text{ kJ mol}^{-1}$ [33] was used. The pertinent parameters used together with the resulting revised calibration constants have been included in Table 8.

The second-law enthalpy of dissociation reported by Hilpert and Ruthart [27] at mid-temperature of their study was converted to 0 K and is given in Table 10. The ion intensity data of germanium and germanium dimer given by Viswanathan et al. [28], were also treated by the second-law

Table 10
Second- and third-law enthalpies in kJ mol^{-1} of the reaction, $\text{Ge}_2(\text{g}) = 2\text{Ge}(\text{g})$

Reference	Temperature range (K)	No. of points	T_M	Second-law, ΔH_{TM}°	Second-law, ΔH_0°	Third-law, $\Delta H_0^{\circ a}$	Selected ΔH_0°
Series 1	1533–1744	15	1632	277.3 ± 9.1	257.4 ± 9.1	264.4 ± 1.2	262.1
Series 2	1351–1664	21	1491	287.7 ± 6.4	268.7 ± 6.4	262.0 ± 1.8	264.2
[22]	1300–1370	2	1334			256.2 ± 4.3^b	256.2
[23]	1370	1	1370			264.8	264.8
[24]	1860–1920	2	1890			246.3 ± 2.7^b	246.3^c
[25]	1537–1941	14	1716	292.2 ± 4.4	271.8 ± 4.4	263.3 ± 1.4	266.1
[26]	1578–2060	17	1787	277.3 ± 6.1	256.5 ± 6.1	253.3 ± 2.0	254.4
[2], Sc–Ge–Ag	1496–2178	25	1744	289.8 ± 5.1	269.1 ± 5.1	255.8 ± 3.3	260.2
[2], Pd–Ge–Ag	1427–1946	49	1647	287.5 ± 2.9	267.5 ± 2.9	255.0 ± 1.8	259.2
[2], Ni–Ge–Ag	1576–2003	32	1764	274.8 ± 5.6	254.1 ± 5.6	255.6 ± 2.1	255.1
[27]	1609–1808	42 ^d	1709	285.4 ± 8.8	265.4 ± 8.8		265.4
[28]	1629–1786	8	1704	287.9 ± 16.1	267.6 ± 16.1		267.6
Weighted average							260.7 ± 1.9^e

^a Overall uncertainties estimated as in [21].

^b Deviation of the mean.

^c Not considered in deriving the recommended value.

^d Read from the second-law plot given in [27].

^e Standard deviation of the weighted average.

method and the enthalpy of dissociation obtained is given in Table 10. The dissociation energy reported by Neckel and Sodeck [29] could not be reevaluated due to lack of original intensity data.

For each set of measurements the selected ΔH_0° value in Table 10 is the weighted average of second- and third-law values whenever both are available (weight of 2 for the third-law value and 1 for the second-law value) and either the second- or third-law value, when only one of them is available. The recommended dissociation energy $D_0^\circ = 260.7 \pm 6.8 \text{ kJ mol}^{-1}$ or $D_{298.15}^\circ = 264.1 \pm 6.8 \text{ kJ mol}^{-1}$ is the weighted average of such selected values, the weight for each selected value taken proportional to the square root of number of points. The overall uncertainty was taken the same as that derived for the present investigation. The dissociation energy derived from the re-evaluated data of Drowart et al. [24] was not considered in the calculation of the recommended value due to the large deviation from the other values.

The enthalpy of formation of Ge_2 was derived from the recommended dissociation energy in combination with the enthalpy of formation of Ge(g) [17] as $\Delta_f H_0^\circ\{\text{Ge}_2(\text{g})\} = 482.7 \pm 6.8 \text{ kJ mol}^{-1}$, or $\Delta_f H_{298.15}^\circ\{\text{Ge}_2(\text{g})\} = 484.8 \pm 6.8 \text{ kJ mol}^{-1}$.

The $D_0^\circ(\text{Ge}_2)$ value of $260.7 \pm 6.8 \text{ kJ mol}^{-1}$ obtained in the present investigation is almost the same as the value of $260.4 \pm 7.0 \text{ kJ mol}^{-1}$ obtained by Kingcade et al. [2]. The previously assessed literature value by Gurvich et al. [18] for $D_0^\circ(\text{Ge}_2)$ is $260.0 \pm 10 \text{ kJ mol}^{-1}$.

The thermal functions of Ge_2 calculated based on the available experimental molecular parameters [9] are in very close agreement with those derived in the present study; the difference in the enthalpy increments and Gibbs energy functions being $\sim 0.7\%$ and $\sim 0.04\%$. These differences result in the second- and third-law enthalpies of dissociation being different by 0.5 and 0.1 kJ mol^{-1} , respectively.

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