

Theoretical and Experimental Investigations of the Ga₂ MoleculeIrene Shim,^{*,†} Kim Mandix,Chemical Physics, Chemistry Department B, The Technical University of Denmark, DTH 301,
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All-electron ab initio Hartree-Fock (HF), multiconfiguration self-consistent-field (CASSCF), and configuration interaction (CI) calculations have been carried out to determine the low-lying electronic states of the Ga₂ molecule. Six states, bound relative to the ²P ground-term Ga atoms, have been identified in the CI calculations. The Ga₂ molecule has a ³Π_u electronic ground state, and the next higher lying states are ³Σ_g⁺, ¹Σ_g⁺, ¹Π_u, ¹Δ_g, and ²Σ_g⁺. The calculated vibrational frequency for the ³Π_u ground state, 175 cm⁻¹, compares well with the experimental value of 180 cm⁻¹. The six lowest lying electronic states have been rationalized in a simple molecular orbital diagram. On the basis of wave functions determined in valence CI calculations, the oscillator strengths have been computed for selected dipole-allowed transitions. Our calculated transition energies and oscillator strengths compare favorably with the available absorption and emission spectra of Ga₂. An approximate treatment of the spin-orbit coupling in the low-lying electronic states of the Ga₂ molecule has been carried out. The four lowest lying spin-orbit coupled states, 0_u⁻, 0_u⁺, 1_u, 2_u, are essentially the split ³Π_u state. The next higher lying state, 0_g⁺, exhibits a double minimum due to the mixing of the states ³Σ_g⁺ and ¹Σ_g⁺. The dissociation energy of the Ga₂ molecule has been determined from the high-temperature mass spectrometric data combined with the experimental vibrational frequency and the spin-orbit coupled electronic states from the present work as D₀⁰ = 110.3 ± 7 kJ mol⁻¹.

I. Introduction

The metallic group III dimers, Al₂, Ga₂, In₂, and Tl₂ have been subjects of several experimental¹⁻⁷ and theoretical⁸⁻¹⁶ investigations. The Al₂ molecule is the most studied of these molecules, but until recently even the symmetry of its electronic ground state had been uncertain. However, the most extensive investigations of Al₂^{9,10} indicate that the molecule has a ³Π_u(pσ_g¹pπ_u¹) ground state with a ³Σ_g⁺(pπ_u²) state located within approximately 200 cm⁻¹ of the ground state. The heavier group III dimers, Ga₂,¹¹ In₂,¹² and Tl₂,^{13,14} are also predicted as having ³Π_u electronic ground states. However, spin-orbit coupling splits the ³Π_u states into 0_u⁻, 0_u⁺, 1_u, and 2_u, and in the case of the molecules In₂ and Tl₂ the resulting ground states are predicted as 0_u⁻. In addition, all three molecules, Ga₂, In₂, and Tl₂ have a low-lying electronic state of ³Σ_g⁺ symmetry.

In the present work we have undertaken combined theoretical and experimental investigations of the Ga₂ molecule in order to study the nature of the chemical bond and also to determine a more accurate value of the dissociation energy of the molecule than has been done in the previous investigations.^{2,3} Our theoretical work includes investigations of all the low-lying electronic states of the Ga₂ molecule dissociating into ²P ground-term Ga atoms. The results of this work will be utilized in a subsequent paper¹⁷ to describe the Ga₃ molecule by employing a diatomics-in-molecules approach. It is interesting to compare the results as obtained in the present work with those of ref 11, since our work is all-electron calculations while Balasubramanian uses an effective core potential.

The Ga₂ molecule has been investigated by performing all-electron ab initio Hartree-Fock (HF), multiconfiguration self-consistent-field (CASSCF), and configuration interaction (CI) calculations and also by carrying out high-temperature mass spectrometric measurements. The electronic structure and the nature of the chemical bond have been elucidated through the theoretical work, and the resulting data have been utilized to derive the partition function of the molecule needed to determine the dissociation energy from the mass spectrometric data.

The HF calculations for the Ga₂ molecule have been performed in the Hartree-Fock-Roothaan formalism.¹⁸ The program MOLECULE¹⁹ has been utilized to calculate the integrals, and for

the HF calculations we have utilized the ALCHEMY program system.²⁰ The CI calculations have been carried out by using ALCHEMY in conjunction with ENERGY²¹ for generating the symbolic energy expressions. The oscillator strengths of the selected optical transitions have been derived by using the program PEDICI.²²

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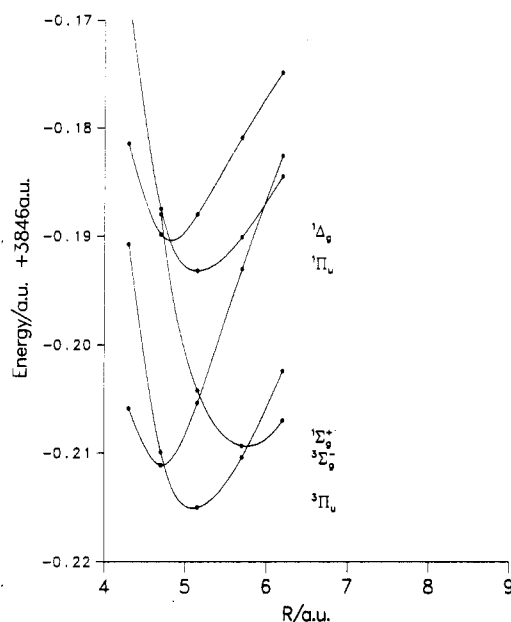


Figure 1. Potential energy curves for five low-lying electronic states of Ga_2 , as obtained in CASSCF calculations.

Finally, the multiconfiguration self-consistent-field calculations have been performed by using the CASSCF program.²³⁻²⁶

II. Theoretical Investigations

A. HF and CASSCF Calculations on Selected Electronic States of the Ga_2 Molecule. In the present work the wave functions have been expanded in terms of Gaussian type functions centered on the Ga atoms. The basis set for the Ga atom is essentially the (14s, 11p, 5d) basis optimized by Huzinaga,²⁷ but the radial densities associated with the most diffuse s and p functions have been contracted slightly. Thus, the exponents of the most diffuse s functions have been altered from (0.18671257, 0.064029371) to (0.295, 0.105), and those of the most diffuse p functions from (0.23851552, 0.069699475) to (0.250, 0.105), respectively. In addition a diffuse d function with exponent 0.2122 has been added. The primitive basis set (14s, 11p, 6d) has been contracted to (8s, 6p, 3d) by using a segmented contraction scheme.

The above-described basis set has been utilized to perform HF and CASSCF calculations on selected states of the Ga_2 molecule.

According to Moore's tables²⁸ the Ga atom has a $^2\text{P}(4s^2 4p^1)$ ground term separated by 24 237.75 cm^{-1} from the first excited term, $^2\text{S}(4s^2 5s^1)$. This indicates that the electronic ground state of the Ga_2 molecule should be sought among the states: $^1\Sigma_g^+(4p\sigma_g^2)$, $^3\Pi_u(4p\sigma_g^1 4p\pi_u^1)$, $^3\Sigma_g^-(4p\pi_u^2)$, and $^1\Sigma_g^+(4p\pi_u^2)$. In the present work we have performed HF calculations on the three first-mentioned states at the internuclear distance 5.00 au. These calculations have revealed that the Ga_2 molecule most likely has a $^3\Pi_u$ ground state. In the HF approximation this state was found to be 0.55 eV more stable than the $^3\Sigma_g^-$ state, and 0.72 eV more stable than the $^1\Sigma_g^+$ state at the internuclear distance 5.00 au. Furthermore, all three states are bound relative to the free HF atoms. The $^3\Pi_u$ state is bound by 1.24 eV, the $^3\Sigma_g^-$ state by 0.69 eV, and the $^1\Sigma_g^+$ state by 0.52 eV.

In addition to the HF calculations we have performed CASSCF calculations on the three above-mentioned states, $^3\Pi_u$, $^3\Sigma_g^-$, and $^1\Sigma_g^+$, as well as on the states $^1\Pi_u$ and $^1\Delta_g$. The calculations have been carried out in the subgroup D_{2h} of the full symmetry group, $D_{\infty h}$, of the molecule. They allowed full reorganization within the

TABLE I: Mulliken Population Analyses of Valence Orbitals of the $^3\Pi_u$ Ground State and Low-Lying Excited States $^3\Sigma_g^-$ and $^1\Sigma_g^+$ of the Ga_2 Molecule^a

state	orb.	overlap pop.	orb. analyses			occupn no.
			s	p	d	
$^3\Pi_u$	$7\sigma_g$	0.46	0.97	0.03	0.01	2
	$8\sigma_g$	0.13	0.02	0.48	0.00	1
	$7\sigma_u$	-0.37	0.91	0.08	0.00	2
	$4\pi_u$	0.22	0.00	0.48	0.02	1
	tot.	0.45	7.90	13.07	10.03	
$^3\Sigma_g^-$	$7\sigma_g$	0.45	0.97	0.03	0.00	2
	$7\sigma_u$	-0.42	0.93	0.07	0.00	2
	$4\pi_u$	0.42	0.00	0.98	0.02	2
	tot.	0.47	7.90	13.07	10.03	
$^1\Sigma_g^+$	$7\sigma_g$	0.55	0.90	0.09	0.01	2
	$8\sigma_g$	0.18	0.11	0.88	0.01	2
	$7\sigma_u$	-0.32	0.90	0.10	0.01	2
	tot.	0.41	7.91	13.07	10.02	

^aThe wave functions have been derived in HF calculations at the internuclear distance 5.00 au.

TABLE II: Mulliken Population Analyses of Valence Orbitals of the $^3\Pi_u$ Ground State and Low-Lying Excited States $^3\Sigma_g^-$ and $^1\Sigma_g^+$ of the Ga_2 Molecule^a

state	orb.	overlap pop.	orb. analyses			occupn no.
			s	p	d	
$^3\Pi_u$	$7\sigma_g$	0.46	0.92	0.05	0.01	1.95
	$8\sigma_g$	0.12	0.03	0.47	0.00	1.00
	$7\sigma_u$	-0.32	0.88	0.07	0.00	1.90
	$8\sigma_u$	-0.04	0.00	0.01	0.00	0.03
	$4\pi_u$	0.19	0.00	0.50	0.00	1.03
	$4\pi_g$	-0.01	0.00	0.04	0.00	0.09
	tot.	0.41	7.83	13.15	10.02	
$^3\Sigma_g^-$	$7\sigma_g$	0.44	0.93	0.04	0.01	1.95
	$8\sigma_g$	0.01	0.00	0.04	0.00	0.09
	$7\sigma_u$	-0.32	0.87	0.07	0.00	1.88
	$8\sigma_u$	-0.02	0.00	0.01	0.00	0.02
	$4\pi_u$	0.36	0.00	0.95	0.02	1.93
	$4\pi_g$	-0.02	0.00	0.06	0.00	0.13
	tot.	0.46	7.81	13.17	10.02	
$^1\Sigma_g^+$	$7\sigma_g$	0.76	0.44	0.53	0.02	1.98
	$8\sigma_g$	-0.06	0.52	0.41	0.00	1.87
	$7\sigma_u$	-0.26	0.86	0.08	0.01	1.90
	$8\sigma_u$	-0.04	0.00	0.01	0.00	0.03
	$4\pi_u$	0.01	0.00	0.06	0.00	0.12
	$4\pi_g$	-0.01	0.00	0.04	0.01	0.10
	tot.	0.43	7.83	13.14	10.03	

^aThe wave functions have been derived in CASSCF calculations at the internuclear distance 5.15 au.

4s and 4p shells of the molecule, and the number of configurations included in each symmetry species of D_{2h} ranges from 136 to 192.

The CASSCF calculations have been performed as functions of the internuclear distance, and Figure 1 shows the potential energy curves obtained.

Tables I and II show Mulliken population analyses of the valence orbitals of the states $^3\Pi_u$, $^3\Sigma_g^-$, and $^1\Sigma_g^+$ as derived in the HF and in the CASSCF calculations, respectively. Comparison between the results presented in the tables reveals only minor differences between the wave functions obtained in the HF and in the CASSCF calculations for the states $^3\Pi_u$ and $^3\Sigma_g^-$. In the $^1\Sigma_g^+$ state the orbitals $7\sigma_g$ and $8\sigma_g$ obtained in the CASSCF calculations are mixtures of the corresponding HF orbitals. However, since these orbitals are practically fully occupied, the differences observed basically reflect an unitary transformation of the wave function. Finally, it is noted that the total numbers of s, p, and d electrons associated with each Ga atom are practically independent of the state considered. This indicates that it should be possible to describe all three states by performing CI calculations based on a common set of molecular orbitals.

In order to avoid favoring any of the molecular states, we decided to optimize the molecular orbitals for the average con-

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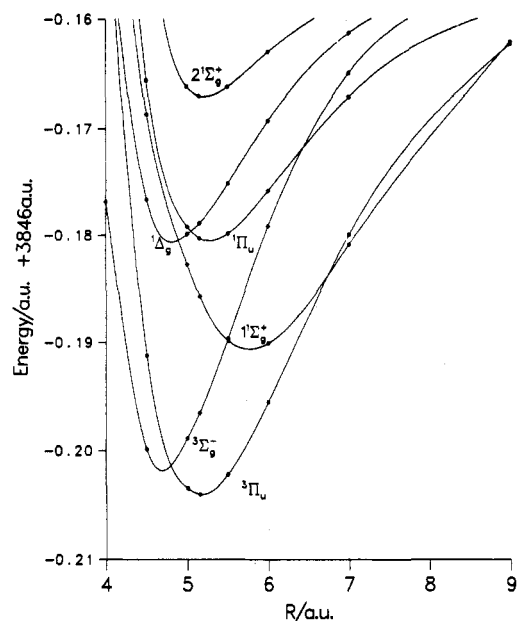


Figure 2. Potential energy curves for the six lowest lying electronic states of Ga₂, as obtained in valence CI calculations.

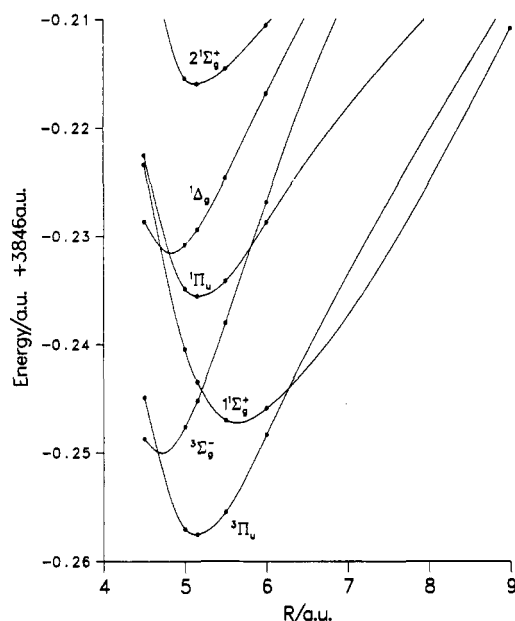


Figure 3. Potential energy curves for the six lowest lying electronic states of the Ga₂ molecule, as derived in CI calculations after correcting for basis-set superposition errors.

figuration ($4p\sigma_g^{1/3}4p\pi_u^{2/3}4p\sigma_u^{1/3}4p\pi_g^{2/3}$). This is analogous to our previous work concerning the molecules Si₂ and Ge₂.²⁹ Thus, for Si₂ and Ge₂ the molecular orbitals optimized for the valence shell configuration ($p\sigma_g^1p\pi_u^1p\sigma_u^1p\pi_g^1$) have been used successfully to describe all the low-lying electronic states of these molecules.

B. Results of CI Calculations on the Ga₂ Molecule. Potential Energy Curves for Low-Lying States. On the basis of the results obtained for the Ga₂ molecule at the internuclear distance 5.15 au as described in the Appendix, it was decided to investigate the potential energy curves for the low-lying electronic states by performing the valence CI calculations, and also the larger CI calculations involving CI matrices with dimensions ranging from 1119 to 1626. In the Appendix the valence CI calculations are designated (II) while the larger CI calculations are labeled (IV). All the low-lying electronic states arising from the interaction between two ²P ground-term Ga atoms have been described by

TABLE III: Spectroscopic Constants for Low-Lying Electronic States of the Ga₂ Molecule as Derived in Valence CI and CASSCF Calculations^a

state	equilib dist, au	transn energy, cm ⁻¹	vib freq, cm ⁻¹	dissocn energy, ^b eV
Valence CI				
³ Π _u	5.16	0	172	1.12
¹ ³ Σ _g ⁻	4.69	617	215	1.07
¹ Σ _g ⁺	5.76	2927	131	0.78
¹ Π _u	5.27	5161	147	0.50
¹ Δ _g	4.86	5226	174	0.50
² ¹ Σ _g ⁺	5.13	8129	151	0.14
¹ Σ _u ⁻	c			
¹ ³ Δ _u	c			
¹ ³ Σ _u ⁺	c			
¹ ³ Π _g	c			
³ Σ _u ⁻	4.94	21153	183	
¹ Π _g	c			
² ³ Π _g	5.65	29425	132	
² ³ Σ _u ⁺	c			
² ³ Σ _g ⁻	6.19	29470	131	
² ³ Δ _u	4.67	29805	257	
CASSCF				
³ Π _u	5.14	0	174	
³ Σ _g ⁻	4.65	831	223	
¹ Σ _g ⁺	5.71	1233	136	
¹ Π _u	5.19	4725	159	
¹ Δ _g	4.80	5398	184	

^a The states are listed according to increasing energy at the internuclear distance 5.15 au. ^b Derived as the difference between the total molecular energies at the equilibrium distance and at the internuclear distance 18 au and corrected for basis-set superposition errors. ^c Repulsive.

carrying out valence CI calculations. In addition, the six lowest lying bound electronic states have been investigated by performing the larger CI calculations. The resulting potential energy curves are shown in Figures 2 and 3, respectively.

The potential energies obtained in the valence CI as well as in the CASSCF calculations have been fitted to Morse curves. In Table III the equilibrium distances, the vibrational frequencies, and the transition energies obtained in the fitting process are reported. In addition we have included the dissociation energies for the bound states obtained from the valence CI calculations. Since the valence CI calculations allow for proper dissociation into ground-term Ga atoms, the dissociation energies have been derived as the differences between the energies of the Ga₂ molecule at the equilibrium distance and at the internuclear distance 18.00 au, but corrected for basis set superposition errors.

Comparison between Figures 1 and 2 reveals striking similarities between the potential energy curves as obtained in the CASSCF calculations and in the valence CI calculations. First of all, the sequence of the low-lying electronic states is identical. For both sets of calculations it is noted that the equilibrium distances of the states ³Σ_g⁻ and ¹Δ_g are pronouncedly less than that of the ³Π_u ground state, whereas the equilibrium distance of the ¹Σ_g⁺ state is larger. However, Table III shows that there are quantitative differences between the results obtained in the valence CI and in the CASSCF calculations. Thus, as compared to the valence CI calculations, the CASSCF calculations cause slight contractions of the bond lengths ranging from 0.02 to 0.08 au, and also small increments, between 2 and 12 cm⁻¹, of the vibrational frequencies.

The most conspicuous difference between the results obtained in the CASSCF and in the valence CI calculations is the relative stabilization of the ¹Σ_g⁺ state in the CASSCF calculations. This is presumably due to the change of configuration occurring in this state. At internuclear distances less than 5 au the major configuration of the ¹Σ_g⁺ state is $(4p\pi_u)^2$, whereas it changes to $(4p\sigma_g)^2$ for internuclear distances larger than 5 au.

Altogether the valence CI calculations based on a single set of molecular orbitals optimized for an average configuration offer a reasonable description of the low-lying electronic states of the Ga₂ molecule. As compared to the CASSCF calculations, the

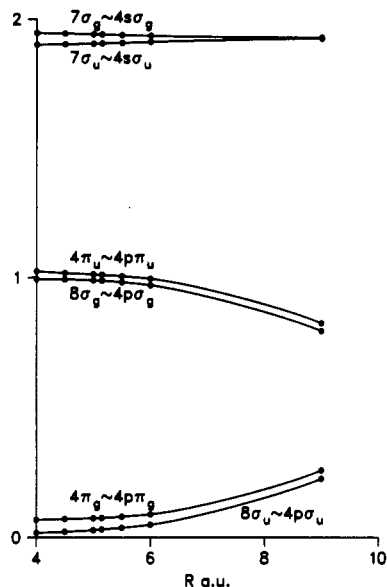


Figure 4. Populations of selected natural valence orbitals for the $^3\Pi_u$ ground state of Ga_2 as functions of internuclear distance. The wave functions were derived in CI calculations containing 1580 configurations.

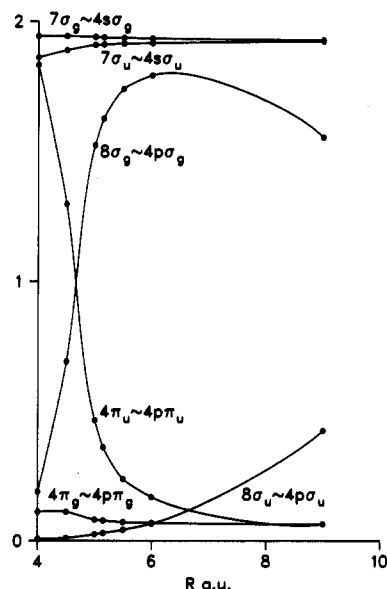


Figure 5. Populations of selected natural valence orbitals for the lowest lying $^1\Sigma_g^+$ state of Ga_2 as functions of internuclear distance. The wave functions were derived in CI calculations containing 1626 configurations.

valence CI calculations require considerably fewer computational resources, and in addition, the valence CI calculations give an overview of the entire spectrum of low-lying electronic states. However, to achieve greater accuracy it is necessary to perform more extensive calculations such as CASSCF and/or larger CI calculations especially for electronic states, such as the $^1\Sigma_g^+$ state, where the valence CI calculations exhibit substantial mixing of configurations.

The occupations in the natural orbitals of the $^3\Pi_u$ ground state and of the lowest lying $^1\Sigma_g^+$ state as derived in the larger CI calculations are displayed in Figures 4 and 5 as functions of the internuclear distance. In accordance with our results derived in the valence CI calculations, Figure 5 shows a change of configuration in the $^1\Sigma_g^+$ state between the internuclear distances 4.5 and 5.0 au. Thus, the results of the larger CI calculations confirm our findings in the valence CI calculations. In addition, for both states, $^3\Pi_u$ and $^1\Sigma_g^+$, only one virtual orbital acquires a population larger than 0.01e, i.e. the $4d\pi_u$ orbital, which mainly accounts for the angular correlation of the 4s and 4p electrons.

The potential energies obtained in the larger CI calculations have been fitted to Morse curves, both uncorrected and corrected

TABLE IV: Spectroscopic Constants for Low-Lying Bound Electronic States of the Ga_2 Molecule as Derived from CI Calculations IV with Counterpoise Corrections^a

state	equilib dist, au	transn energy, cm^{-1}	vib freq, cm^{-1}
$^3\Pi_u$	5.15	0	175
$^3\Sigma_g^-$	4.69	1641	217
$^1\Sigma_g^+$	5.65	2156	152
$^1\Pi_u$	5.19	4804	161
$^1\Delta_g$	4.81	5682	189
$2^1\Sigma_g^+$	5.16	9101	161
$0_u^+0_g^+(^3\Pi_u)$	5.15	0	175
$1_u(^3\Pi_u)$	5.15	260	175
$2_u(^3\Pi_u)$	5.15	551	175
$0_g^+(1)$	4.69, 5.65	1876, 2507	214, 140
$1_g(^3\Sigma_g^-)$	4.69	1918	251
$0_g^+(2)$	5.25	3189	337
$1_u(^1\Pi_u)$	5.19	5096	162
$2_g(^1\Delta_g)$	4.81	5959	189
$0_g^+(3)$	5.15	9424	159

^a Also included are the results obtained in the approximate spin-orbit-coupling treatment.

for basis set superposition errors by applying the counterpoise method.³⁰ Correcting for the basis-set superposition errors, however, only causes modest changes in the spectroscopic constants derived in the fitting processes. Thus, for the six lowest lying states the equilibrium distances increase by 0.02–0.05 au and the vibrational frequencies decrease by 3–8 cm^{-1} .

Table IV presents the spectroscopic constants, i.e. equilibrium distances, vibrational frequencies, and transition energies derived by fitting the potential energies corrected for the basis-set superposition errors to Morse curves. Also included are the corresponding data derived by taking into account the spin-orbit coupling between the low-lying states.

The sequence of the low-lying electronic states of the Ga_2 molecule can be rationalized in a simple molecular orbital diagram in which the $4p\sigma_g$ orbital is slightly more stable than the $4p\pi_u$ orbital. The energy difference between the orbitals $4s\sigma_g$ and $4p\pi_u$ should be so small that the exchange energy gained by uncoupling the spins of two electrons in the $4p\sigma_g$ orbital is larger than the loss in energy due to the difference in orbital energies when one electron is placed in the $4p\sigma_g$ and the other in the $4p\pi_u$ orbital. Such an orbital diagram is consistent with the $^3\Pi_u(4p\sigma_g^1 4p\pi_u^1)$ state being more stable than the $^3\Sigma_g^-(4p\pi_u^2)$ state, which in turn is more stable than the $^1\Sigma_g^+(4p\sigma_g^2)$ state.

Spin-Orbit Coupling of Low-Lying Electronic States. The effect of the spin-orbit coupling on the six low-lying bound electronic states of the Ga_2 molecule has been investigated by carrying out perturbational treatments based on the Hamiltonian $H' = \sum_i \xi(r_i) \vec{l}_i \cdot \vec{s}_i$. The radial integrals needed for evaluating the matrix elements of H' have been assumed equal, and the value of 550.83 cm^{-1} has been obtained from Moore's tables.²⁸ The energies of the LS states have been added to the appropriate diagonal elements of the matrices representing the spin-orbit coupling for each value of Ω , and the spin-orbit-coupled states have been derived by diagonalization of the matrices.

The spin-orbit-coupling treatments have been performed as functions of the internuclear distance, and Figure 6 shows the potential energy curves obtained. Fitting the potential energies to Morse curves has resulted in the spectroscopic constants reported in Table IV.

The four lowest lying spin-orbit-coupled states, 0_u^- , 0_u^+ , 1_u , and 2_u , are essentially the split $^3\Pi_u$ state. The states $1_u(2)$ and 2_u arise from the LS states $^1\Pi_u$ and $^1\Delta_g$, respectively. In the two lowest lying 0_g^+ states change of configurations occur at approximately 5.15 au, and this gives rise to a double minimum in the lowest lying 0_g^+ state. It is noted that the symmetry of the ground state is consistent with the findings for the molecules In_2 ¹² and Tl_2 .^{13,14}

TABLE V: Measured Ion Currents and Derived Third-Law Enthalpies for the Reaction Ga₂(g) → 2Ga(g)

T, K	ion intens, A ^a				log K _p	-Δ(G _T ^o - H ₀ ^o)/T, J K ⁻¹ mol ⁻¹	ΔH ₀ ^o , kJ mol ⁻¹
	⁶⁹ Ga ⁺		¹⁴⁰ Ga ₂ ⁺				
1349	5.78	(-9)	1.90	(-13)	0.0484	80.37	107.2
1302	2.86	(-9)	6.80	(-14)	-0.1319	80.06	107.5
1379	9.29	(-9)	4.21	(-13)	0.1246	80.56	107.8
1384	9.12	(-9)	4.05	(-13)	0.1269	80.59	108.2
1348	4.96	(-9)	1.56	(-13)	0.0008	80.37	108.3
1357	5.77	(-9)	1.87	(-13)	0.0564	80.42	107.7
1378	8.26	(-9)	3.24	(-13)	0.1359	80.56	107.4
1327	3.73	(-9)	9.60	(-14)	-0.0041	80.23	107.5
1393	9.09	(-9)	3.64	(-13)	0.1732	80.65	107.7
1400	1.07 ₃	(-8)	4.70	(-13)	0.2085	80.69	107.4
1422	1.32 ₃	(-8)	6.01	(-13)	0.2904	80.82	107.0
1415	1.17 ₈	(-8)	4.44	(-13)	0.3189	80.78	105.7
1303	2.77	(-9)	7.10	(-14)	-0.1781	80.07	108.8
1419	1.45 ₇	(-9)	6.66	(-13)	0.3287	80.80	105.7
1447	1.88 ₈	(-8)	1.11	(-12)	0.3400	80.96	107.7
1436	1.70 ₂	(-8)	9.18	(-13)	0.3295	80.90	107.1
1291	2.28	(-9)	5.00	(-14)	-0.1981	79.98	108.2
1327	4.07	(-9)	9.80	(-13)	0.0241	80.23	105.8
1332	4.35	(-9)	1.01	(-13)	0.0704	80.26	105.1
1434	1.64	(-8)	8.81	(-13)	0.3145	80.89	107.4
							107.3 ± 1.0 ^b

^aNumbers in parentheses represent powers of ten. ^bAverage.

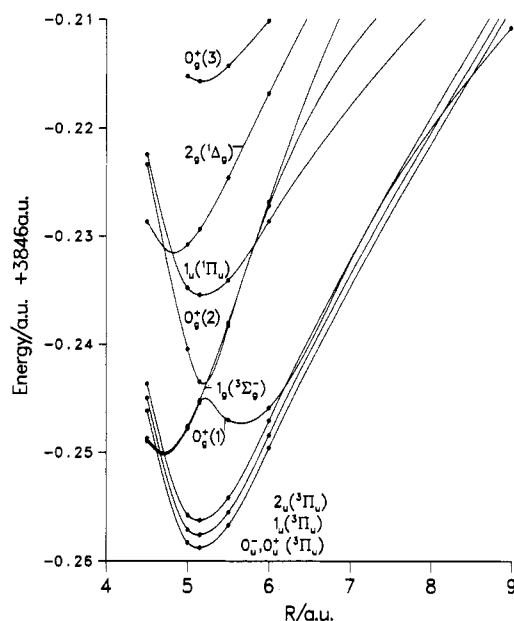


Figure 6. Potential energy curves for the ten lowest lying spin-orbit-coupled states of the Ga₂ molecule.

III. Mass Spectrometric Equilibrium Measurements

The equilibrium measurements have been performed by using a 90°-sector, 12-in. radius magnetic focusing mass spectrometer equipped with a Knudsen cell assembly. The instrument and experimental procedure have previously been described.³¹ The 99.999% gallium was contained in a graphite Knudsen cell that in turn was inserted into a molybdenum Knudsen cell. The orifice diameter was 0.7 mm and the combined orifice length was 1 mm.

Heating of the sample was effected by radiation from a thoriated tungsten resistance heater surrounding the Knudsen cell. The temperatures were measured by sighting on a black body cavity in the base of the molybdenum cell. The optical pyrometer used had previously been calibrated in situ at the melting point of an NBS reference gold sample contained in a graphite Knudsen cell. The molecular beam effusing from the sample cell into the ion source region of the mass spectrometer was ionized with 15-V electrons; the electron emission current was 1.0 mA. The ionic species were identified by their mass-to-charge ratios, isotopic

TABLE VI: Gibbs Energy Functions, -(G_T^o - H₀^o)/T (J K⁻¹ mol⁻¹), and Heat Content Functions, H_T^o - H₀^o (kJ mol⁻¹), for Ga₂(g)

T, K	-(G _T ^o - H ₀ ^o)/T	H _T ^o - H ₀ ^o	T, K	-(G _T ^o - H ₀ ^o)/T	H _T ^o - H ₀ ^o
298.15	226.6	10.24	1300	284.3	49.53
1000	273.8	37.47	1400	287.2	53.57
1100	277.6	41.48	1500	290.0	57.62
1200	281.1	45.50	1600	292.6	61.66

abundances, shutter profiles, and ionization efficiencies. The appearance potential of Ga₂⁺ was evaluated from the ionization efficiency curve as 5.9 ± 0.2 eV by the linear extrapolation method, using the ionization potential of the Ga atom of 6.00 eV as reference.²⁸ Despite the gallium sample being contained in a reducing graphite cell, Ga₂O⁺ was observed in the effusing vapor, the intensity of which decreased relative to that of Ga and Ga₂ in the course of the investigation. During the initial measurements, at temperatures below the limit of measurement for primary Ga₂⁺, it was observed that under the conditions of the investigation 3% of the Ga₂O fragmented into Ga₂⁺. Thus in the course of the investigation the intensity of Ga₂O⁺ was measured at each temperature together with that of Ga⁺ and Ga₂⁺ and a correction applied to the measured Ga₂⁺ signal to account for the fragment contribution from Ga₂O. This correction varied from 20% of the total signal of Ga₂⁺ during the early measurements at the lower temperatures to about 3% during the measurements later in the investigation.

The measured multiplier ion currents I_i⁺ for ⁶⁹Ga⁺ and ¹⁴⁰Ga₂⁺, the latter after correction for fragment contribution from Ga₂O, are listed in Table V. These ion currents were related to the corresponding partial pressures, P_i, according to the relation P_i = k_iI + T. The instrument constant, k_{Ga}, was determined from data sets measured for Ga⁺ at different temperatures during the early stages of the investigation and from the published vapor pressure data of Hultgren et al.³² The calibration constant for the dimer, k_{Ga₂}, has been evaluated from the relation k_{Ga₂} = k_{Ga}(σ_{Ga}γ_{Ga}n_{Ga})/(σ_{Ga₂}γ_{Ga₂}n_{Ga}). Here the relative ionization cross section σ_{Ga₂} of Ga₂ has been taken as 0.75 multiplied by the sum of the relative atomic cross section of Ga³³ and the relative multiplier gain γ_{Ga}/γ_{Ga₂} (taken as 1.0, assuming cancellation of the mass effect and the molecular effect). The resulting k_i values in atm A⁻¹ K⁻¹ are: Ga, 3.940, and Ga₂, 3.294, respectively.

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The Gibbs energy functions, $-(G_T^\circ - H_{298}^\circ)/T$, and heat content functions, $H_T^\circ - H_{298}^\circ$, for atomic gallium were taken from Hultgren et al.³² For the Ga₂ molecule these thermal functions were calculated according to statistical thermodynamic procedures using the harmonic oscillator rigid rotator approximation.³⁴ The molecular constants used are $\omega_e = 180 \text{ cm}^{-1}$; $r_e = 2.72 \text{ \AA}$; as well as the spin-orbit coupled electronic states (Table IV). The symmetry number used is the weighted average according to the isotropic abundance of the symmetric and asymmetric Ga₂ isotopomers. The resulting values are listed in Table VI.

The dissociation energy of gaseous Ga₂ was obtained from the experimental equilibrium constants, K_p , for the gas-phase reaction



The enthalpy change, ΔH_0° , for reaction 1 was calculated by the third-law method, $\Delta H_0^\circ = -RT \ln K_p - T\Delta[(G_T^\circ - H_0^\circ)/T]$, yielding $\Delta H_0^\circ = 107.3 \pm 1.0 \text{ kJ mol}^{-1}$. The experimental results are included in Table V. The enthalpy change for reaction 1 was also evaluated from a least-squares analysis of a plot of $\log K_p$ vs $1/T$, (second-law method), yielding an enthalpy change at the average temperature of 1365 K of $\Delta H_{1365}^\circ = 124.5 \pm 6.3 \text{ kJ mol}^{-1}$. The uncertainties given correspond to the standard deviation. The corresponding enthalpy change referenced to 0 K is $\Delta H_0^\circ = 113.4 \text{ kJ mol}^{-1}$.

We select $\Delta H_0^\circ = 110.3 \pm 7 \text{ kJ mol}^{-1}$ for the dissociation enthalpy of diatomic gallium, giving equal the weight to the second- and third-law values for reaction 1. Here the uncertainty given takes into account the errors in the experimental measurements of ion intensities, temperatures, and fragmentation as well as the errors in the pressure calibration and thermal functions.

IV. Comparison with Literature Data

Our theoretical work confirms the results of ref 11 with respect to the symmetry of the electronic ground state, $^3\Pi_u$, as well as of the lowest lying excited state, $^3\Sigma_g^-$. In addition, many of the quantitative differences observed have been remedied through the erratum.¹¹ Thus, except for the $2^1\Sigma_g^+$ state there is reasonable agreement between the equilibrium distances and the vibrational frequencies of the low-lying electronic states. However, the sequences of some of the low-lying electronic states have been interchanged.

In the present work the $1^1\Sigma_g^+$ state is found to be the third lowest electronic state while it is the fourth in ref 11, i.e. the $1^1\Sigma_g^+$ state is located above the $1^1\Pi_u$ state. Using equivalent computational methods to describe the low-lying electronic states by In₂, Balasubramanian and Li¹² found the $1^1\Sigma_g^+$ state of In₂ to be above the $1^1\Pi_u$ state. However, the sequence of the three lowest lying states of the Ga₂ molecule as determined in the present work is in accordance with those found for the group III dimers Al₂⁸ and Tl₂.¹⁴ Thus, for Al₂ Basch et al.⁸ have found that the $1^1\Sigma_g^+$ state is slightly more stable than the $1^1\Pi_u$ state, and for the Tl₂ molecule Christiansen¹⁴ determined the $1^1\Sigma_g^+(0^+, \text{III})$ state to be 1350 cm^{-1} below the $1^1\Delta_g(2_g)$ state and 2500 cm^{-1} below the $1^1\Pi_u(1_u)$ state.

The vibrational frequencies of the low-lying electronic states derived in the present work are all higher than the corrected values obtained in ref 11 by $17\text{--}36 \text{ cm}^{-1}$. It is noted however, that our ω_e value for the $^3\Pi_u$ ground state, 175 cm^{-1} , is in good agreement with the experimental value of 180 cm^{-1} .⁷

Since the present work has been carried out before Balasubramanian's erratum was published, we were concerned about the discrepancies between the calculated equilibrium distances. However, the equilibrium distances of the six lowest lying electronic states of Ga₂ as determined in our work are in reasonable agreement with the corrected values obtained by Balasubramanian.¹¹ In his work the relativistic effects are included through the use of a relativistic pseudopotential, but the lack of relativistic effects in the present work should not cause any significant discrepancies between the calculated equilibrium distances. Usually

TABLE VII: Vertical Transition Energies, Oscillator Strengths, and Polarizations of Dipole-Allowed Transitions from the Four Lowest Lying States of the Ga₂ Molecule as Derived from Valence CI Calculations (II)

transn	vert transn energy, cm^{-1}		osc strength, au	polzn
	a	b		
$1^3\Sigma_g^- \leftarrow ^3\Pi_u$	1643	1006	0.0004	x, y
$1^3\Pi_g \leftarrow ^3\Pi_u$	16531	17548	0.0310	z
$2^3\Pi_g \leftarrow ^3\Pi_u$	29900	30038	0.0165	z
$2^3\Sigma_g^- \leftarrow ^3\Pi_u$	32735	33698	0.0006	x, y
$1^3\Sigma_g^- \leftarrow ^3\Sigma_g^-$	21436	20042	0.0332	z
$2^3\Sigma_g^- \leftarrow ^3\Sigma_g^-$		34836	0.0431	z
$1^1\Pi_u \leftarrow ^1\Sigma_g^+$	2188	774	0.0004	x, y
$2^1\Sigma_g^+ \leftarrow ^1\Pi_u$	2931	2883	0.0034	x, y
$1^1\Pi_g \leftarrow ^1\Pi_u$	16222	18020	0.0691	z
$2^1\Pi_g \leftarrow ^1\Pi_u$	36336	35622	0.0027	z

^a Vertical transition energies from the $^3\Pi_u$ and $1^1\Pi_u$ states are reported at 5.15 au, those from $^3\Sigma_g^-$ at 4.50 au, and the transition from $1^3\Sigma_g^-$ at 5.50 au. ^b At 5.00 au.

the alterations of bond lengths in diatomic molecules caused by the relativistic effects reflect the relativistic changes of the charge densities of the atomic orbitals. In the case of the Ga atom Desclaux's tables³⁵ show that the relativistic contraction or expansion of the orbitals 3s, 3p, and 3d amounts to less than 0.01 au. The orbitals 4s and $4p_{1/2}$ contract approximately 0.03 au while the $4p_{3/2}$ orbital expands less than 0.01 au. Thus, the relativistic effects should only cause minor changes.

Table VII shows the vertical transition energies for some dipole-allowed transitions from the four lowest lying electronic states. Also included are the oscillator strengths derived on the basis of the valence CI wave functions. On the whole, our calculated transition energies and oscillator strengths support the assignments of the known spectra as reported by Balasubramanian.¹¹ Thus, our calculated transition energy of 20042 cm^{-1} for the $1^3\Sigma_g^- \leftarrow ^3\Sigma_g^-$ transition agrees well with the emission spectra observed by Ginter et al.⁴ In addition, Table VII reveals that this transition is also associated with an appreciable oscillator strength.

The absorption spectra of Ga₂ isolated in inert gas matrices have been measured by Douglas et al.⁵ These authors observed a broad band centered at 15592 cm^{-1} and a more narrow band at 29934 cm^{-1} . In accordance with Balasubramanian's and the present work the observed transitions most likely are $1^3\Pi_g \leftarrow ^3\Pi_u$ and $2^3\Pi_g \leftarrow ^3\Pi_u$. These assignments are consistent with the transition energies as well as the calculated oscillator strengths reported in Table VII. Furthermore, the shapes of the observed lines are consistent with the $1^3\Pi_g$ state being repulsive and the $2^3\Pi_g$ state being bound.

The dissociation energy, as derived from the valence CI calculations corrected for basis set superposition errors amounts to 1.12 eV. This is in very good agreement with our experimental value of 1.14 eV. In order to derive the experimental value from the measured mass spectrometric data, we have utilized the calculated equilibrium distance of the $^3\Pi_u$ ground state, 5.15 au, together with the experimental value for the vibrational frequency, 180 cm^{-1} ⁷ for deriving the rotational and the vibrational partition functions of the Ga₂ molecule. In addition, the low-lying spin-orbit-coupled electronic states have been utilized to determine the electronic contribution to the partition function of Ga₂. On this background, and because of our more numerous mass spectrometric data points, our experimentally determined dissociation energy is more accurate than the previous values.^{1-3,36} The difference in our selected value of $110.3 \pm 7 \text{ kJ mol}^{-1}$ and the selected literature value of 135 kJ mol^{-1} comes mainly from the different thermal functions used. Thus with the thermal functions used previously,³⁶ the third-law enthalpy changes by 22 kJ mol^{-1} , which would bring the literature value to 112 kJ mol^{-1} in good

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TABLE VIII: Contributions Larger than 0.3% to the Wave Functions Describing the ³Π_g Ground State and Lowest Lying ¹Σ_g⁺ State of the Ga₂ Molecule at Internuclear Distance 5.15 au

state	confign										contribn in CI calcn, ^a %			
	4s _g	4s _u	4p _{σ_g}	4p _{σ_u}	4p _{π_u}	4p _{π_g}	4d _{π_u}	4d _{δ_g}	4d _{π_g}	5p _{π_u}	I	II	III	IV
³ Π _u	2	2	1	0	1	0					97.9	90.9	90.8	88.2
	2	2	0	1	0	1					2.1	1.0	0.9	0.7
	2	1	1	1	1	0						1.2	1.2	0.8
	2	1	2	0	0	1						1.6	1.5	1.0
	2	0	1	0	1	2						1.0	1.0	0.7
	1	1	1	0	2	1						1.9	1.9	1.4
	2	1	0	0	2	1						0.3	0.3	0.2
	2	0	1	0	3	0						0.5	0.5	0.4
	0	2	1	0	3	0						0.5	0.5	0.4
	1	2	1	0	1	0		1						0.3
	1	2	0	0	2	0				1				0.4
	2	1	0	0	1	1	1							0.4
¹ Σ _g ⁺	2	2	2	0	0	0					85.9	75.2	80.5	74.6
	2	2	0	0	2	0					12.4	16.3	10.8	13.7
	2	2	0	2	0	0					1.4	0.9	0.9	0.7
	2	2	0	0	0	2					0.4	0.5	0.3	0.2
	2	1	1	0	1	1						1.8	1.6	1.4
	2	0	2	0	0	2						1.1	1.1	0.8
	1	1	2	0	1	1						1.7	1.9	1.3
	0	2	2	0	2	0						0.3	0.4	0.3
	1	2	1	0	1	0	1							1.1
	2	1	1	0	1	0			1					0.3
	2	1	1	0	0	1	1							0.5

^aThe CI calculations (I, II, III, IV) involve (2, 192, 394, 1580) configurations for the ³Π_g state and (4, 176, 500, 1626) configurations for the ¹Σ_g⁺ state.

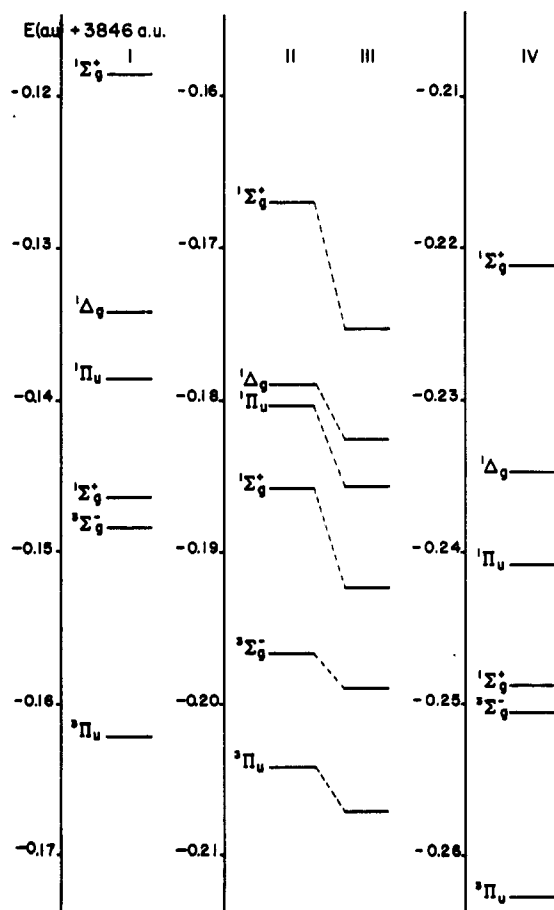


Figure 7. Energies of the six lowest lying electronic states, as derived in the different CI calculations described in the text.

agreement with our selected value.

V. Conclusions

In the present work we have presented results of both theoretical and experimental investigations of the gaseous Ga₂ molecule. The electronic states and the nature of the chemical bond in Ga₂ have

TABLE IX: Mulliken Population Analyses of Valence Orbitals of the ³Π_g Ground State and Lowest Lying ³Σ_g⁻ and ¹Σ_g⁺ States of the Ga₂ Molecule at Internuclear Distance 5.15 au^a

state	orb.	overlap pop.	orb. analyses			occupn no.
			s	p	d	
³ Π _g	7σ _g	0.44	0.92	0.04	0.00	1.94
	8σ _g	0.12	0.03	0.47	0.00	0.99
	4π _u	0.19	0.00	0.50	0.01	1.01
	5π _u	0.00	0.00	0.00	0.01	0.02
	7σ _u	-0.34	0.89	0.06	0.00	1.90
	8σ _u	-0.03	0.00	0.01	0.00	0.03
	4π _g	-0.01	0.00	0.04	0.00	0.08
tot.		0.37	7.84	13.12	10.04	
³ Σ _g ⁻	7σ _g	0.43	0.93	0.04	0.01	1.94
	8σ _g	0.01	0.00	0.03	0.00	0.07
	4π _u	0.36	0.00	0.94	0.01	1.92
	7σ _u	-0.33	0.88	0.06	0.00	1.89
	8σ _u	-0.02	0.00	0.01	0.00	0.02
	4π _g	-0.02	0.00	0.06	0.00	0.11
tot.		0.43	7.82	13.15	10.04	
¹ Σ _g ⁺	7σ _g	0.45	0.92	0.04	0.00	1.94
	8σ _g	0.21	0.04	0.76	0.01	1.63
	4π _u	0.06	0.00	0.18	0.00	0.36
	5π _u	0.00	0.00	0.00	0.01	0.02
	7σ _u	-0.34	0.89	0.06	0.01	1.91
	8σ _u	-0.03	0.00	0.01	0.00	0.03
	4π _g	-0.01	0.00	0.04	0.00	0.08
tot.		0.33	7.86	13.10	10.04	

^aThe wave functions have been derived in CI calculations (IV) involving 1580 configurations for ³Π_g, 1484 for ³Σ_g⁻, and 1626 for ¹Σ_g⁺.

been elucidated through all-electron ab initio HF, CASSCF, and CI calculations.

The dissociation energy of the Ga₂ molecule has been determined from the high-temperature mass spectrometric data by utilizing the experimental vibrational frequency, 180 cm⁻¹ in conjunction with the calculated equilibrium distance and low-lying spin-orbit-coupled electronic states to derive the partition function of the molecule. The experimental dissociation energy of the Ga₂ molecule as determined in the present work is D₀[°] = 110.3 ± 7 kJ mol⁻¹.

Our ab initio work has confirmed Balasubramanian's predictions¹¹ that the molecule has a ³Π_g electronic ground state, and

a low-lying electronic state of $^3\Sigma_g^-$ symmetry. However, in contrast to Balasubramanian's results,¹¹ we find the third electronic state to be $^1\Sigma_g^+$. The six lowest lying electronic states of the Ga_2 molecule arise from the configurations $(4p\sigma_g^2 4p\pi_u^1)$, $(4p\pi_u^2)$, and $(4p\sigma_g^2)$, respectively. The sequence of the low-lying electronic states is consistent with a simple molecular orbital diagram involving the orbitals $4p\sigma_g$ and $4p\pi_u$. In this diagram the $4p\pi_u$ orbital should be slightly more stable than the $4p\sigma_g$ orbital.

Our calculated transition energies and oscillator strengths are consistent with the observed electronic spectra of the Ga_2 molecule.^{4,5}

Acknowledgment. The authors thank Mr. M. J. Stickney for his assistance in the mass spectrometric equilibrium measurements and Ms. H. C. Finkbeiner for her help in their evaluation. The ab initio calculations have been performed at UNI-C, the Technical University of Denmark. The work at Texas A&M University has been supported by the Robert A. Welch Foundation and the National Science Foundation. I.S. and K.A.G. appreciate the support by NATO Grant No. RG0268/89 for international collaboration in research.

Appendix: Various CI Calculations for the Ga_2 Molecule at the Internuclear Distance 5.15 au

The molecular orbitals optimized for the average configuration $(4p\sigma_g^{1/3} 4p\pi_u^{2/3} 4p\sigma_u^{1/3} 4p\pi_g^{2/3})$ at the internuclear distance 5.15 au have been utilized in a variety of CI calculations to describe the low-lying electronic states of the Ga_2 molecule. As in the case of the CASSCF calculations, the CI calculations have been performed in the subgroup D_{2h} of the full symmetry group $D_{\infty h}$ of the molecule.

In Figure 7 and Table VIII we present some of the results of the CI calculations. Figure 7 shows the relative energies of the six lowest lying electronic states of the Ga_2 molecule as derived in four different sets of CI calculations, and Table VIII contains analyses of the wave functions for the $^3\Pi_u$ ground state as well as for the lowest lying $^1\Sigma_g^+$ state.

The complexity of the wave functions associated with Figure 7 and Table VIII increases from left to right. In the simplest calculations (I) the $4s\sigma_g$ and $4s\sigma_u$ orbitals are kept doubly occupied, and the two 4p electrons are distributed in all possible ways in the molecular orbitals arising from the 4p atomic orbitals. Although this gives rise to very small CI matrices, ranging from the dimensions 2 to 6, all the configurations needed to allow the molecule to dissociate properly into two ground term atoms are included. Moving left in Figure 7 and Table VIII, the next set of CI calculations (II) are valence CI calculations that allow full reorganization within the valence shells of the molecule, i.e. within the orbitals $4s\sigma_g$, $4s\sigma_u$, $4p\sigma_g$, $4p\pi_u$, $4p\pi_g$, $4p\sigma_u$. These calculations

corresponds to the CASSCF calculations, and the dimensions of the CI matrices range from 136 to 192. The third set of CI calculations (III) are valence CI calculations augmented by full correlation of the 4p electrons within the basis set used. In this case the dimensions of the CI matrices are between 322 and 500. Finally, the fourth set of CI calculations (IV) have been derived from the third set by adding single and double excitations from the $4s\sigma_g$ and $4s\sigma_u$ orbitals of the dominant configurations into the 20 lowest lying virtual orbitals. The virtual orbitals include 4 orbitals of σ_g symmetry, 2 of π_u , 1 of δ_g , 4 of σ_u , 2 of π_g , and 1 of δ_u . The states $^1\Sigma_g^+$ and $^1\Delta_g$ belong to the same representation of D_{2h} , and for these states single and double excitations from the $4s\sigma_g$ and $4s\sigma_u$ orbitals have been included from the reference configurations $(4s\sigma_g^2 4s\sigma_u^2 4p\sigma_g^2)$ and $(4s\sigma_g^2 4s\sigma_u^2 4p\pi_u^2)$. In the case of the states $^3\Pi_u$ and $^1\Pi_u$ the reference configuration is $(4s\sigma_g^2 4s\sigma_u^2 4p\sigma_g^1 4p\pi_u^1)$, while it is $(4s\sigma_g^2 4s\sigma_u^2 4p\pi_u^2)$ for the $^3\Sigma_g^-$ state. The CI matrices in these calculations have dimensions ranging from 1119 to 1626.

Table VIII reveals that relative to CI calculation I, CI calculations II and III essentially introduce angular correlation of the 4s electrons, while CI calculation IV includes angular and radial correlations of the 4s electrons. Furthermore, it is noted that the mixing between the two major configurations of the $^1\Sigma_g^+$ state, i.e. $(4p\sigma_g^2)$ and $(4p\pi_u^2)$, is sensitive to the amount of correlation included.

Figure 7 shows that the symmetries and the sequences of the six lowest lying electronic states are identical in the four sets of CI calculations. Furthermore, the six states are exactly those arising from the configurations $(4p\sigma_g^1 4p\pi_u^1)$, $(4p\sigma_g^2)$, and $(4p\pi_u^2)$.

The finer details in Figure 7 reveal that the energy range covered by the six lowest lying electronic states decreases from 1.19 eV in CI calculation I, to 1.01 eV and 0.87 eV in CI calculations II and III, while it increases to 1.13 eV in CI calculation IV. Thus, it is interesting to note that the relative energies of the six lowest lying states are almost identical in the smallest and in the largest CI calculations, (I) and (IV). In addition it is noted that the different amounts of correlation included in the CI calculations mainly influence the energy splittings between states arising from different orbital configurations, such as $^3\Pi_u(4p\sigma_g^1 4p\pi_u^1)$ and $^3\Sigma_g^-(4p\pi_u^2)$.

Table IX shows the Mulliken population analyses for the three lowest lying states as derived in the largest CI calculations (IV) at the internuclear distance 5.15 au. Although the CI calculations are based on a single set of molecular orbitals it is noted that there are striking similarities between the population analyses of Table IX and those of Tables I and II derived from the HF and CASSCF wave functions of each state.

Registry No. Ga_2 , 74508-24-0.