

# Electronic Structure and Thermodynamic Properties of LaC<sub>2</sub>

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Ab initio self-consistent field (SCF), Møller–Plesset second-order perturbation theory (MP2), complete active space multiconfiguration self-consistent field (CASSCF) followed by multireference singles and doubles configuration interaction (MRSDCI), and relativistic configuration interaction (RCI) studies to include the spin–orbit effects were carried out on LaC<sub>2</sub>. The enthalpy of the La(g) + 2C(graph) = LaC<sub>2</sub>(g) reaction as well as the atomization and dissociation (La–C<sub>2</sub>) energies were computed for the theoretically determined structure. The experimental Gibbs energy functions (GEF) were corrected by using the symmetrical C<sub>2v</sub> structure instead of the assumed (incorrect) unsymmetrical linear geometry. The corrected experimental enthalpies thus obtained agree with the theoretically computed results.

## 1. Introduction

The nature of the transition metal–carbon bonding is fundamental to several areas such as surface chemistry, catalysis, astrochemistry, fullerene chemistry, etc. In recent years, transition metal atoms trapped inside carbon cages such as buckminsterfullerene are known to yield stable species that can be isolated in macroscopic quantities.<sup>1</sup> The metallofullerenes and metallocarbohedranes are examples of such species which are readily generated by doping carbon clusters with metal atoms.<sup>1</sup>

Lanthanum carbides are among the stable gaseous carbides observed in the pioneering work of Chupka et al.<sup>2</sup> Since then, a large amount of work has been devoted to the transition metal carbides<sup>3</sup> including studies on LaC, La<sub>2</sub>C,<sup>4</sup> LaC<sub>n</sub> (*n* = 2–8),<sup>5,6</sup> La<sub>2</sub>C<sub>n</sub> (*n* = 2–8)<sup>7,8</sup> as well as the bimetal LaIrC<sub>n</sub> (*n* = 1–4) carbides.<sup>3</sup> The principal data concerning the gaseous carbides obtained up to now pertain to the atomization energies as obtained by the Knudsen effusion technique combined with mass spectrometry.<sup>9,10</sup> Because of the lack of structural data, the thermodynamic functions of LaC<sub>n</sub> needed for the evaluation of enthalpies of La(g) + *n*C(graph) = LaC<sub>n</sub>(g) reactions were calculated from the estimated molecular parameters. Based on the pseudo-oxygen character of the C<sub>2</sub> group,<sup>2,11</sup> a linear unsymmetrical structure was assumed for the LaC<sub>2</sub> molecule.

Clemmer et al.<sup>12</sup> have studied the bonding of metals to carbon rings using mass spectrometry on LaC<sub>n</sub><sup>+</sup> isomers. These authors have noted that in LaC<sub>n</sub><sup>+</sup> clusters for even *n* the La is inserted into the ring, while for odd *n*, the La appears to be attached outside or inside the carbon ring. The spectra also exhibited odd/even alternations.

In spite of several experimental studies on transition metal carbide clusters, there is little information on the structure and nature of bonding in these species. The objective of this investigation is to fill this wide gap by a detailed theoretical ab initio relativistic study on LaC<sub>2</sub>. In this work, we present our computed results of the geometry search for a number of possible low-lying electronic states by applying extended ab initio approaches that include both relativistic and electron correlation effects. Using the computed molecular structure, we have calculated the atomization and dissociation energies of LaC<sub>2</sub> as well as the Gibbs free energy functions. The nature

of the metal–carbon bonds in the formation of the molecule was analyzed through the Mulliken populations. The experimental thermodynamic data such as the Gibbs free energy functions, enthalpies of formation, etc., were corrected by using the computed molecular structure of LaC<sub>2</sub>. The results thus obtained agree with the computed results.

## 2. Method of Calculations

The calculations were performed using ab initio approaches that included electron correlation effects such as Møller–Plesset second-order perturbation theory (MP2),<sup>13</sup> complete-active-space-multiconfiguration self-consistent-field (CASSCF),<sup>14</sup> and multireference singles and doubles configuration interaction methods including the Davidson correction.<sup>15</sup> Geometries were optimized at the MP2 and CASSCF levels of theory by a quasi Newton–Raphson procedure<sup>16,17</sup> and by a stepwise method at the configuration interaction levels. The vibrational frequencies were calculated at the MP2 and CASSCF levels.

All the calculations described here were made using the relativistic effective core potentials (RECPs) that retained the 5s<sup>2</sup>5p<sup>6</sup>5d<sup>1</sup>6s<sup>2</sup> shells in the valence space for lanthanum,<sup>18</sup> and 2s<sup>2</sup>2p<sup>2</sup> valence shells of the carbon atoms.<sup>19</sup> The most diffuse exponents in the original basis set have been left uncontracted leading to (5s4p3d) and (3p3s) valence basis sets for Y and C, respectively. The carbon basis set was supplemented with a six-component 3d Gaussian function from Dunning and Hay.<sup>20</sup>

The MP2 calculations were performed using the spin-unrestricted Hartree–Fock method.<sup>21</sup> The projected values (free from contaminations due to other states) from the MP2 calculations are reported. All 19 outermost electrons of LaC<sub>2</sub> were correlated in this method.

The CASSCF calculations included six a<sub>1</sub>, three b<sub>1</sub>, two b<sub>2</sub>, and one a<sub>2</sub> orbitals for the nonlinear C–La–C structure, and five a<sub>1</sub>, three b<sub>1</sub>, three b<sub>2</sub>, and one a<sub>2</sub> orbitals for the linear La–C–C structure that correspond to the valence orbitals of La and 2p orbitals of C in the active space. The calculations were performed in C<sub>2v</sub> symmetry (*z* being the main axis). Seven electrons (La 5d<sup>1</sup>6s;<sup>2</sup> and C 2p<sup>2</sup>) were distributed in all possible ways in the active space. The La(5s, 5p) and C(2s) orbitals were allowed to relax at the CASSCF stage, but no excitations from these orbitals were allowed. The above choice of active space leads to about 14 000 configuration state functions (CSF).

Configuration interaction calculations were carried out following the CASSCF calculations using the multireference

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**TABLE 1: Calculated Geometries and Total Energies for the Symmetrical ( $C_{2v}$ ) and Linear ( $C_{\infty v}$ ) Structures in the  $^2A_1$  and  $^2\Sigma^+$  Ground Electronic States of  $LaC_2$ , Respectively<sup>a</sup>**

structure	property	method			
		SCF	MP2	CASSCF	MRSDCI
$C_{2v}$ $^2A_1$	La—C	2.388	2.367	2.384	2.388
	C—C	1.251	1.283	1.276	1.283
	$\angle CLaC$	30.38	31.44	31.05	32.40
	$E$ (au)	-41.93224	-42.35239	-42.06422	-42.09778
	$\mu$ (D)	8.54	8.15	8.08	7.90
$C_{\infty v}$ $^2\Sigma^+$	La—C	2.253	2.247	2.223	2.111
	C—C	1.292	1.273	1.277	1.286
	$E$ (au)	-41.87770	-42.27229	-42.04991	-42.07225
	$\mu$ (D)	12.77	12.74	10.16	10.68
	$\Delta E^a$ (eV)	1.48	2.81	0.39	0.69

<sup>a</sup> Distances are in angstroms, and angles in degrees. <sup>b</sup> Energy separation  $\Delta E = E_{C_{2v}} - E_{C_{\infty v}}$ .

singles and doubles (MRSDCI) method to include higher-order electron correlation effects. All configurations in the CASSCF with coefficients  $\geq 0.07$ , important for equilibrium as well as for dissociated molecules, were included as reference configurations in the MRSDCI. All possible single and double excitations arising from the seven outermost electrons were allowed from these reference configurations. The MRSDCI calculations included up to 530 000 CSFs.

Following the MRSDCI calculations, relativistic configuration interaction (RCI) calculations, which included the low-lying electronic configurations of different spatial and spin symmetries in the presence of the spin-orbit operator, were carried out to estimate the spin-orbit contribution to the atomization energies. The configurations corresponding to the low-lying states were used as reference configurations along with singly and doubly excited configurations from the reference configurations. The calculations were performed for the  $C_{2v}$  structure and included 56 reference configurations corresponding to doublets and quartets of  $A_1$ ,  $B_1$ ,  $B_2$ , and  $A_2$  symmetry. The seven outermost electrons were distributed among 11  $a_1$ , 6  $b_1$ , 5  $b_2$ , and 3  $a_2$  orbitals.

The calculations of the thermodynamic functions have been performed at the MP2 and CASSCF levels of theory by applying the ideal gas, rigid rotor, and harmonic oscillator approximations.<sup>22</sup>

The MP2 computations were made using the Gaussian 94<sup>23</sup> code. The CASSCF computations were made using the GAMESS<sup>24</sup> program package and also a modified version of ALCHEMY II<sup>25</sup> to include the RECPs.<sup>26</sup> The MRSDCI computations were made using ALCHEMY II. The RCI computations were based on the general RCI method for polyatomics.<sup>27</sup>

### 3. The $C_{2v}$ vs Linear Structure of the Ground State of $LaC_2$

The geometry of gaseous  $LaC_2$  has not yet been determined experimentally, and the structural data needed for the evaluation of experimental enthalpies has been based on the assumed similarity of the  $LaC_2$  molecule to the Y—O interactions.<sup>6</sup> The theoretical search for the equilibrium structures has been performed for a number of electronic states of the symmetrical  $C_{2v}$  and unsymmetrical linear  $LaC_2$  complexes.

The ground state of  $LaC_2$  is a  $^2A_1$  electronic state with a symmetrical  $C_{2v}$  geometry, while the linear unsymmetrical complex has a  $^2\Sigma^+$  state as the lowest electronic state. Geometry optimizations for these structures have been performed at various levels of theory as shown in Table 1, with the objective of seeking semiquantitative levels of accuracy. All the methods

**TABLE 2: Atomization Enthalpies ( $\Delta H^\circ_{a,0}$ ), Enthalpies of the  $La(g) + 2C(gr) = LaC_2(g)$  Reaction and Dissociation Energies ( $D^\circ_0(La-C)$ ) for Symmetrical ( $C_{2v}$ ) and Unsymmetrical ( $C_{\infty v}$ ) Structures of  $LaC_2$ <sup>a</sup>**

method	geometry	$\Delta H^\circ_{a,0}$	$\Delta H^\circ_0$	$D^\circ_0$
SCF	$C_{2v}$	783.22	639.18	
	$C_{\infty v}$	640.01	782.39	
MP2	$C_{2v}$	1200.88	221.52	606.59
	$C_{\infty v}$	990.58	431.82	
CASSCF	$C_{2v}$	1086.69	335.71	637.6
	$C_{\infty v}$	1049.13	373.26	
MRSDCI	$C_{2v}$	1170.91	251.49	658.07
	$C_{\infty v}$	1104.04	318.76	
experiment		$1263 \pm 5$	$159.3 \pm 4^b$	$664^b$
		1263–1229	159–193 <sup>c</sup>	
		1260	162–161 <sup>d</sup>	

<sup>a</sup> All energies in kJ/mol. <sup>b</sup> Reference 5. <sup>c</sup> Reference 2. <sup>d</sup> Reference 6.

employed here agree well on the prediction of the molecular parameters. All levels of theory give the  $C_{2v}$  structure as the global minimum in the potential energy surface of the  $LaC_2$  molecule, although the energy separation between the  $C_{2v}$  structure and the linear structure varies significantly.

The experimental values of the  $La-C_2$  dissociation and atomization energies have been evaluated previously<sup>5,6</sup> from the third and second law methods using an assumed unsymmetrical linear geometry. In the present work the same quantities are calculated theoretically. As evidenced from Table 2, the agreement between the theoretical and experimental energies is good, if electron correlation effects are included to a significant extent (MP2, MRSDCI). The theoretical enthalpies are sensitive to the structure of the molecule. The calculated enthalpies for the linear complex exhibit significantly worse agreement with experiment when compared to those of the  $C_{2v}$  structure. The zero point vibrational energy correction calculated at the MP2 level amounts to 14.8 kJ/mol ( $C_{2v}$ ) and 14.0 kJ/mol ( $C_{\infty v}$ ), and when applied to the atomization energies, lowers our best  $\Delta H^\circ_{a,0}$  (MP2) to 1185.2 kJ/mol.

The main contribution for the spin-orbit interaction in  $LaC_2$  comes from the La atom since it is the heaviest atom present. The main change in the electron density during the formation of the  $La-C$  bonds is the transfer of electronic charge density from the La atom to the carbons. The spin-orbit energy lowering for the  $LaC_2$  ground state formation can be estimated as the difference of the spin-orbit effects in the La atom and  $La^+$  cation. The energy lowering in La amounts<sup>28</sup> to 631.9  $cm^{-1}$  and in  $La^+$  to 1183.3  $cm^{-1}$ . The estimated value of the spin-orbit correction for the  $La(g) + 2C(gr) = LaC_2(g)$  reaction enthalpy is 550  $cm^{-1}$  (6.6 kJ/mol), which is so small that it does not have a significant effect on the thermodynamic properties of  $LaC_2$ .

The relativistic configuration interaction calculations were made for the  $^2A_1$  ground electronic state of  $LaC_2$ . The lowest configurations corresponding to  $^4A_1$ ,  $^4B_1$ ,  $^4B_2$ ,  $^4A_2$ ,  $^2B_1$ ,  $^2B_2$ , and  $^2A_2$  electronic states mix less than 1% with the ground state, and the spin-orbit correction lowers the energy of the molecule near its equilibrium geometry by 1 kJ/mol.

### 4. Nature of Chemical Bonding in the Ground and Excited States

Due to a number of low-lying excited states of the La atom and the proximity of the singlet and triplet states of  $C_2$ , the  $LaC_2$  molecule possesses a number of excited states with their equilibrium energies below the La and  $C_2$  dissociation limit. All the doublet states considered here have been found to be more stable than the corresponding quartet states. In most cases,

**TABLE 3: Optimized Geometries, Energy Separations, and Dissociation Energies for the Excited Electronic States of the LaC<sub>2</sub> Symmetrical C<sub>2v</sub> Structure Calculated within the CASSCF Approach**

	<sup>4</sup> A <sub>1</sub>	<sup>2</sup> B <sub>1</sub>	<sup>4</sup> B <sub>1</sub>	<sup>2</sup> B <sub>2</sub>	<sup>4</sup> B <sub>2</sub>	<sup>2</sup> A <sub>2</sub>	<sup>4</sup> A <sub>2</sub>
La–C	2.844	2.400	2.705	2.428	2.796	2.409	2.873
C–C	1.312	1.273	1.274	1.277	1.283	1.265	1.303
∠CLaC	26.67	30.76	27.24	30.50	26.52	30.45	26.23
<i>E</i>	−41.96458	−42.01325	−41.95943	−42.02318	−41.96249	−42.01779	−41.92989
Δ <i>E</i>	2.71	1.39	2.85	1.12	2.77	1.26	3.65
<i>D</i> <sup>o</sup> <sub>0</sub>	376.0	503.8	362.5	529.9	370.5	515.7	284.9

<sup>a</sup> Distances in Å, angles in deg, separation energies in eV, and dissociation energies in kJ/mol.

**TABLE 4: Optimized Geometries, Energy Separations, and Dissociation Energies for the Excited Electronic States of the LaC<sub>2</sub> Linear Unsymmetrical Structure Calculated within the CASSCF Approach<sup>a</sup>**

	<sup>4</sup> Σ <sup>+</sup>	<sup>2</sup> Π	<sup>4</sup> Π	<sup>2</sup> Δ	<sup>4</sup> Δ
La–C	2.583	2.541	2.665	2.616	2.601
C–C	1.314	1.310	1.312	1.297	1.313
<i>E</i>	−41.96311	−42.01184	−41.93154	−41.96603	−41.96061
Δ <i>E</i>	2.36	1.04	3.22	2.28	2.43
<i>D</i> <sup>o</sup> <sub>0</sub>	372.1	500.1	289.2	379.8	365.6

<sup>a</sup> Distances in Å angles in deg, separation energies in eV, and dissociation energies in kJ/mol.

**TABLE 5: Atomic Charges, Mulliken Populations, and Dipole Moments (in debyes) of the Low-Lying Electronic States of LaC<sub>2</sub>**

		electronic states				
C <sub>2v</sub>	structure	<sup>2</sup> A <sub>1</sub>	<sup>4</sup> A <sub>1</sub>	<sup>2</sup> B <sub>1</sub>	<sup>2</sup> B <sub>2</sub>	<sup>2</sup> A <sub>2</sub>
La	charge	1.092	0.811	1.085	1.129	1.061
	s	2.828	2.951	2.107	2.096	2.046
	p	6.176	6.249	6.192	6.341	6.002
	d	0.904	0.989	1.616	1.434	1.868
C <sup>a</sup>	charge	−0.546	−0.405	−0.543	−0.565	−0.530
	s	1.788	1.863	1.829	1.779	1.801
	p	2.714	2.508	2.673	2.747	2.684
	d	0.044	0.034	0.041	0.039	0.045
dipole moment		8.08	4.84	9.62	9.33	11.78
C <sub>∞v</sub>	structure	<sup>2</sup> Σ <sup>+</sup>	<sup>2</sup> Π	<sup>2</sup> Δ		
La	charge	0.967	0.787	0.859		
	s	2.964	4.074	3.006		
	p	6.055	6.040	6.128		
	d	1.014	0.099	1.007		
C	charge	−0.937	−0.661	−0.650		
	s	1.568	1.554	1.540		
	p	3.287	3.038	3.036		
	d	0.082	0.068	0.074		
C	charge	−0.031	−0.126	−0.209		
	s	1.658	1.805	1.804		
	p	2.304	2.257	2.342		
	d	0.069	0.064	0.063		
dipole moment		10.16	6.53	7.40		

<sup>a</sup> C represents one of two equivalent atoms.

the La–C bond is 0.3 Å longer in the quartet states than in the doublet states, which indicates a weakening of the bond in the quartet states.

The bonds in the lowest excited states (Tables 3 and 4) are formed as a consequence of charge transfer from La to C<sub>2</sub>. The electronic charge distribution is, however, different in the linear and C<sub>2v</sub> complexes. In the case of the unsymmetrical linear LaC<sub>2</sub> complex, the primary increase in the electronic charge density is on the C atom directly bonded to the La atom, while the other carbon atom not involved in the bonding with La in a direct manner undergoes very little change in the electronic charge distribution. In the C<sub>2v</sub> complex (Table 5), as expected, both carbons undergo the same amount of charge distribution.

**TABLE 6: Leading Configurations of the Low-Lying Electronic States of the Symmetrical C<sub>2v</sub> Structure of LaC<sub>2</sub><sup>a</sup>**

state	coeff	configurations								
		4a <sub>1</sub>	5a <sub>1</sub>	6a <sub>1</sub>	3b <sub>1</sub>	4b <sub>1</sub>	2b <sub>2</sub>	3b <sub>2</sub>	4b <sub>2</sub>	1a <sub>2</sub>
<sup>2</sup> A <sub>1</sub>	0.829	2	2	1	0	0	2	0	0	0
<sup>4</sup> A <sub>1</sub> <sup>b</sup>	0.674	2	2	1	0	0	1	1	0	0
	−0.408	2	2	1	0	0	1	0	1	0
<sup>2</sup> B <sub>1</sub> <sup>b</sup>	0.694	2	2	0	1	0	2	0	0	0
	−0.546	2	2	0	0	1	2	0	0	0
<sup>4</sup> B <sub>1</sub> <sup>a</sup>	0.491	2	1	1	1	0	2	0	0	0
	0.604	2	1	1	0	1	2	0	0	0
<sup>2</sup> B <sub>2</sub> <sup>b</sup>	−0.573	2	2	0	0	0	2	1	0	0
	0.689	2	2	0	0	0	2	0	1	0
<sup>4</sup> B <sub>2</sub> <sup>b</sup>	0.460	2	1	1	0	0	2	1	0	0
	0.587	2	1	1	0	0	2	0	1	0
<sup>2</sup> A <sub>2</sub>	0.918	2	2	0	0	0	2	0	0	1
<sup>4</sup> A <sub>2</sub> <sup>b</sup>	0.729	2	2	0	0	0	1	1	0	1
	−0.444	2	2	0	0	0	1	0	1	1

<sup>a</sup> Only higher occupied orbitals are shown. All lower orbitals are double occupied. <sup>b</sup> These two configurations listed for these states can be transformed into a single-determinantal representation by a suitable orbital transformation.

**TABLE 7: Leading Configurations for the Low-Lying Electronic States of the Unsymmetrical Linear Structure of LaC<sub>2</sub><sup>a</sup>**

state	coeff	configurations				
		5σ	6σ	2π	3π	4π
<sup>2</sup> Σ <sup>+</sup>	0.927	2	1	4	0	0
<sup>4</sup> Σ <sup>+</sup> <sup>b</sup>	0.652	2	1	3	1	0
	0.652	2	1	3	0	1
<sup>2</sup> Π	0.915	2	2	3	0	0
<sup>4</sup> Π	0.649	2	0	3	2	0
	0.651	2	0	3	0	2
<sup>2</sup> Δ <sup>b</sup>	0.865	2	1	3	1	0
	0.337	2	1	3	0	1
<sup>4</sup> Δ <sup>b</sup>	0.641	2	1	3	1	0
	0.641	2	1	3	0	1

<sup>a</sup> Only higher occupied orbitals are shown. All lower orbitals are doubly occupied. <sup>b</sup> These two configurations listed for these states can be transformed into a single-determinantal representation by a suitable orbital transformation.

While in the linear case the La–C bond is formed primarily due to the σ donation from the s and d orbitals of La (with little π back-donation), the π back-donation is significant in the C<sub>2v</sub> case (Table 5).

The molecular wave functions for the bent and linear ground states are single determinantal (Tables 6 and 7). Although some of the excited states in Tables 6 and 7 seem to exhibit two-configurational character, they can be transformed to a single-determinantal wave function through an appropriate choice of orbital transformations. The MP2 method gives very good results for the ground state of LaC<sub>2</sub> primarily due to the single-configurational character of the wave function. The correlation energy is very important for the computation of the enthalpies and dissociation energies as evidenced by the somewhat poor enthalpies computed at the SCF level.

**TABLE 8: Gibbs Energy Function,  $GEF = (G^\circ_T - H^\circ_0)/T$ , and Heat Content Functions,  $\Delta H = H^\circ_T - H^\circ_0$ , Calculated by Various Methods<sup>a</sup>**

method	structure		temp						
			298	2000	2200	2400	2600	2800	3000
CASSCF	$C_{\infty U}$	GEF	-215.3	-273.0	-276.2	-279.1	-281.8	-284.3	-286.6
		$\Delta H$	8.7	65.7	73.0	80.3	87.5	94.9	102.3
	$C_{2U}$	GEF	-231.6	-307.4	-311.6	-315.5	-319.2	-322.5	-325.7
MP2	$C_{\infty U}$	$\Delta H$	10.6	88.9	98.6	108.5	118.3	128.1	138.0
		GEF	-242.6	-317.1	-321.3	-325.2	-328.8	-332.2	-335.3
	$C_{2U}$	$\Delta H$	10.4	88.2	98.0	107.8	117.6	127.4	137.3
		GEF	-239.6	-326.6	-331.6	-336.2	-340.4	-344.4	-348.1
	$C_{\infty U}$	$\Delta H$	11.7	103.9	115.3	126.8	138.3	149.8	161.4
		GEF	-277.0	-315.4	-320.8	-325.8	-330.5	-334.8	-338.9
other <sup>b</sup>	$C_{\infty U}$	$\Delta H$	10.4	113.8	126.5	139.1	151.8	164.4	177.0

<sup>a</sup> GEF in J/kmol,  $\Delta H$  in kJ/mol, temperature in K. <sup>b</sup> Evaluated from estimated molecular parameters (ref 5).

## 5. Thermodynamic Functions for the Ground State of $LaC_2$

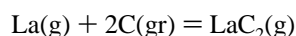
The experimental evaluation of the thermodynamic functions usually proceeds through the second or third law methods.<sup>5,6</sup> These techniques require some knowledge of the structure of the molecule under consideration. A linear unsymmetrical structure ( $La-C-C$ ) was assumed before<sup>5,6</sup> for the purpose of calculating the thermodynamic properties. The force constants were also adjusted for such a linear unsymmetrical structure. As seen from Table 8, although the experimentally estimated Gibbs energy functions agree quite well with our calculated MP2 data, the  $C_{2v}$  geometry is the proper ground state and the GEF's for this structure need to be calculated. The third law enthalpies for the reaction  $La(g) + 2C(gr) = LaC_2(g)$  as a function of temperature are given by the expression<sup>5</sup>

$$\Delta H^\circ_0 = -RT \ln K_p(T) - T\Delta[(G^\circ_T - H^\circ_0)/T]$$

where  $K_p(T)$  is the equilibrium constant and  $\Delta[(G^\circ_T - H^\circ_0)/T]$  is the Gibbs energy function change for the reaction. The Gibbs free energy functions computed theoretically are shown in Table 8. Using the experimental values for the thermodynamic functions for  $C(gr)$  and  $La(g)$ ,<sup>29</sup> the theoretical Gibbs energy functions (Table 8), and the experimental values<sup>5</sup> of  $K_p(T)$ , the reaction enthalpies ( $\Delta H^\circ_0$ ) were recomputed for several temperatures. The results thus obtained for the linear theoretical structure are in excellent agreement with the experimental findings (Table 9). However, when GEF's for the  $C_{2v}$  structure are applied,  $\Delta H^\circ_0$  increases by 25 kJ/mol. This increase improves the agreement between the theoretical and experimental results for the enthalpies and atomization energies.

## 6. Conclusions

The lanthanum-dicarbide system has been a subject of several experimental investigations which yielded the enthalpy of the reaction:



and the atomization and dissociation energies of the gaseous  $LaC_2$  molecule. We obtained optimized geometries and energies for several quartet and doublet electronic states of  $LaC_2$ . This facilitated a more accurate analysis of the experimental thermodynamic data.

The symmetrical  $C_{2v}$  structure in its  $^2A_1$  electronic state has been found to be the ground electronic state of  $LaC_2$ . The molecule exhibits several bound excited electronic states lying below the  $La + C_2$  dissociation energy limit.

The  $La-C$  bonding is highly ionic in all of the electronic states considered here, with a net transfer of electronic charge density from  $La$  to the  $C_2$  fragment. The  $\sigma$ -donation- $\pi$ -back-

**TABLE 9: Gibbs Energy Functions (GEF) Calculated by Various Methods for the  $La(g) + 2C(gr) = LaC_2(g)$  Reaction and the Corresponding Third Law Enthalpies Calculated from Experimental  $K(T)$** 

T	theoretical					
	experimental <sup>b</sup>		linear		$C_{2v}$	
	-GEF	$\Delta H^\circ_0$	-GEF	$\Delta H^\circ_0$	-GEF	$\Delta H^\circ_0$
2248	61.869	158.3	61.893	158.4	72.293	181.8
2310	61.643	159.9	61.584	159.8	72.284	184.5
2404	61.295	159.7	60.509	157.8	71.508	184.2
2492	60.965	160.3	59.410	156.4	71.308	186.1
2609	60.520	159.5	58.679	154.7	71.079	187.0

<sup>a</sup> GEF in J/mol  $\Delta H^\circ_0$  in kJ/mol, temperature in K. <sup>b</sup> Reference 5.

donation model of the chemical bond may be applied although significant  $\pi$ -back donation is present primarily in the  $C_{2v}$  structure.

Different levels of the theory lead to similar equilibrium geometries for the ground state. This observation agrees with the single determinantal structure of the wave function. The calculated enthalpies, however, depend significantly on the amount of the correlation energy included in the calculations. The highest levels of theory considered here, namely, the MRSDCI and MP2 techniques, gave enthalpies close to the experimental values.

The experimental evaluation of enthalpies required some insight into the geometries and force constants. Since the structural data on  $LaC_2$  did not exist, the thermodynamic functions were estimated on the basis of similarity of  $La-O$  and  $LaC_2$  with the assumption that  $LaC_2$  in its ground state would possess a linear unsymmetrical structure. Theoretical calculations, on the other hand, favor a symmetrical bent  $C_{2v}$  structure. We corrected the experimentally estimated enthalpies using the correct structure. The enthalpy of the reaction  $La(g) + 2C(gr) = LaC_2(g)$  increases by 20 kJ/mol when the  $C_{2v}$  structure is considered. The atomization energy decreases by the same extent. In both cases, the agreement between the experimental and theoretical results improves. The spin-orbit effect was found to make only a small contribution to the enthalpies.

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