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Electronic structure and bonding in the RhC molecule by all-electron *ab initio* HF-CI calculations and mass spectrometric measurements

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In the present study we present all-electron *ab initio* Hartree–Fock (HF) and configuration interaction (CI) calculations of the $^2\Sigma^+$ ground state as well as of 16 excited states of the RhC molecule. The calculated spectroscopic constants of the lowest lying states are in good agreement with the experimental data. The chemical bond in the electronic ground state is mainly due to interaction of the $4d$ orbitals of Rh with the $2s$ and $2p$ orbitals of C. The bond is a triple bond composed of two π bonds and one σ bond. The $5s$ electron of Rh hardly participates in the bond formation. It is located in a singly occupied, nonbonding orbital. The chemical bond in RhC is polar with a charge transfer from Rh to C giving rise to a dipole moment of 2.82 D at the experimental equilibrium distance. Mass spectrometric equilibrium measurements over the temperature range 1970–2806 K have resulted in the selected dissociation $D_0^\circ = 576.0 \pm 3.8$ kJ mol^{-1} for RhC(g).

I. INTRODUCTION

Platinum metals and platinum metal alloys are important components of heterogeneous catalysts; for example, in petrol refining, catalytic converters, and in coal gasification and liquification.

In the action of the catalyst with carbon-containing gases at the interface of the platinum metal surface the bond formation between the platinum metal and the carbon must play an important role. The knowledge of the nature of the bond in the smallest chemical unit between carbon and the metal, namely the diatomic platinum metal carbide molecule should therefore be of considerable basic scientific and applied technological interest.

In continuation of our theoretical and experimental investigations of diatomic carbides[1] we present here our results of the molecule RhC.

The RhC molecule has previously been studied by optical spectroscopy both in the gas phase[2-4] and by matrix isolation techniques.[5] The molecule has also been investigated by Knudsen effusion mass spectrometry.[6,7] The optical spectra and the dissociation energy of RhC have been reviewed by Huber and Herzberg.[8]

In the present investigation we have studied the nature of bonding in the RhC molecule by performing all electron *ab initio* Hartree–Fock (HF) and configuration interaction (CI) calculations of the electronic ground state as well as of the low-lying excited states of the molecule.

The HF calculations for the RhC molecule have been carried out in the Hartree–Fock–Roothaan formalism.[9] The integrals have been calculated using the program MOLE-CULE.[10] For the HF calculations we have utilized the AL-CHEMY program system,[11] and the CI calculations have been performed using ALCHEMY in conjunction with the program ENERGY[12] for generating the symbolic energy expressions.

Finally, the deformation density map has been produced using a program especially designed for contour plotting of orbitals, densities, and electrostatic potentials.[13]

We also report detailed thermodynamic equilibrium data on RhC. The derived dissociation energy is presented together with a reevaluation of the mass spectrometric literature data.

II. THEORETICAL INVESTIGATIONS

A. Basis sets and atomic calculations

The basis sets used consisted of Gaussian-type functions. For the Rh atom the basis set was essentially Huzinaga's,[14] but we have extended it by addition of two p functions with exponents 0.20 and 0.09 in order to represent the $5p$ orbital. Furthermore, the exponents of the most diffuse s functions were altered from 0.107 321 68 and 0.038 640 044 to 0.125 and 0.05, respectively. Finally, the primitive basis set $(17s, 13p, 8d)$ has been contracted to $(10s, 8p, 5d)$ using a segmented contraction scheme. In this basis the $4d$ orbital is represented by a triple zeta function while all other orbitals including the empty $5p$ orbital are described by double zeta functions. For the C atom we have utilized Huzinaga's $(10s, 6p)$ basis[15] augmented by a d function with exponent 0.75 as suggested by Dunning and Hay.[16] The basis set for the C atom has been contracted to $(4s, 3p, 1d)$.

In Table I we compare the calculated relative energies of some low-lying terms of the Rh and the C atoms with the corresponding experimental values. It is observed that we obtain the right ordering of the terms, but the calculated splittings are somewhat too large compared to the experimental values. However, the calculated splittings for the Rh atom are in good agreement with those derived in numerical HF calculations,[17] and this certainly implies the good quality of our basis set.

TABLE I. Relative energies (in a.u.) of the lowest-lying terms originating from different orbital configurations of the Rh atom, and also of the lowest-lying terms of the C atom. The calculated energies are results of HF calculations.

Atom	State	Calculated	Experimental[a]
Rh	$^4F(4d)^8(5s)^1$	0.0000	0.0000
Rh	$^2D(4d)^9$	0.0548	0.0126
Rh	$^4F(4d)^7(5s)^2$	0.0746	0.0599
C	$^3P(2s)^2(2p)^2$	0.0000	0.0000
C	$^1D(2s)^2(2p)^2$	0.0573	0.0463
C	$^1S(2s)^2(2p)^2$	0.1392	0.0985

[a] Center of gravity of each multiplet has been calculated from data of C. E. Moore, Natl. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, D. C., 1952), Vols. 1 and 3.

B. HF calculations on selected states of the RhC molecule

The RhC molecule is well-known experimentally, thus it has a $^2\Sigma^+$ ground state, and two components of a $^2\Pi$ state have been observed at 9462.94 and at 10 242.75 cm^{-1} above the ground state, respectively.[8] Both these states can be derived from a C atom in its $^3P(2s)^2(2p)^2$ ground term and a Rh atom either in its $^4F(4d)^8(5s)^1$ ground term or in its $^2D(4d)^9$ first excited term. The $^2D(4d)^9$ term of Rh is only 0.34 eV above the $^4F(4d)^8(5s)^1$ ground term (Table I), and the ^2D term might therefore play an important role for the interaction between the Rh and the C atoms. However, since the ^4F and the ^2D terms originate from different configurations it is *a priori* probable that the difference in correlation errors in the two terms (Table I) will be important for the description of the RhC molecule. The difference in the correlation errors for atomic terms originating from different configurations are known to play important roles in the description of the transition metal dimers, and it has been studied in detail especially for the Ni$_2$ molecule.[18]

TABLE II. HF calculations for the RhC molecule at the internuclear distance 3.05 a.u.

State	Valence shell Configuration						Energy (a.u.)[a]
	2δ	5π	6π	10σ	11σ	12σ	
$^2\Pi$	4	3	0	2	2	2	0.144 9[c]
$^4\Pi$	2	4	1	2	2	2	0.134 7[c]
$^4\Pi$	4	4	1	2	1	1	0.084 9[c]
$^4\Sigma^-$	4	4	2	2	1	0	0.079 3[c]
$^6\Sigma^+$	2	4	2	2	2	1	0.079 2[c]
$^2\Delta$	3	4	0	2	2	2	0.051 4[c]
$^2\Pi,^2\Phi^b$	3	4	1	2	2	1	0.047 291
$^2\Delta$	3	4	2	2	2	0	0.039 374
$^4\Delta$	3	4	2	2	2	0	0.022 012
$^4\Pi,^4\Phi^b$	3	4	1	2	2	1	0.012 861
$^2\Pi$	4	4	1	2	2	0	− 0.001 948
$^2\Sigma^+$	4	4	0	2	2	1	− 0.006 399

[a] Energy of RhC minus energy of the Rh and the C atoms, both in their ground terms.
[b] The wave function represents a mixture of orbital angular momenta.
[c] Derived from calculations not fully converged.

Keeping the correlation problem in mind we decided to perform HF calculations on a variety of states that can be derived from either the $(4d)^8(5s)^1$ or the $(4d)^9$ configurations of Rh. The calculations have all been performed at the internuclear distance 3.05 a.u. which is the equilibrium distance for the RhC molecule in its $^2\Sigma^+$ ground state.[8] In Table II we have presented the results of the HF calculations. Of all the states we investigated it is noted that only a $^2\Sigma^+$ and a $^2\Pi$ state have energies below the sum of the energies of the separated atoms. The $^2\Sigma^+$ state can be regarded as derived from the $(4d)^8(5s)^1$ configuration of Rh, whereas the bound $^2\Pi$ state originates from the $(4d)^9$ configuration. This is reflected in the Mulliken population analyses of the two states shown in Table III. The population analyses show that all the valence orbitals except the 2δ orbitals are considerably delocalized and that the two states have very similar valence orbitals. It is noted that for both states the major contributions to the overlap population are due to the 5π and the 11σ orbitals. The former orbitals consist of a mixture of $d\pi$ on Rh and $p\pi$ on C while the latter are a combination of mainly $d\sigma$ on Rh and $s\sigma$ and $p\sigma$ on C. The 12σ orbital of the $^2\Sigma^+$ state can be regarded as a $5s$ orbital on Rh although some charge has been donated into the $2p\sigma$ on C. For both states the 2δ orbitals are completely localized, and they do not participate in the bond formation.

It is noted that the energy difference between the $^2\Sigma^+$ and the $^2\Pi$ states in the HF approximation is only 976 cm^{-1} as compared to the experimental value of $\sim$10 000 cm^{-1}. This discrepancy indicates that the two states have very different correlation energies, that is, a much larger correlation energy is associated with the $^2\Sigma^+$ state which has the unpaired electron in the σ orbital than with the $^2\Pi$ state where the unpaired electron is in the π orbital.

It is surprising that the $^2\Pi$ state in the HF approximation is found only 976 cm^{-1} above the $^2\Sigma^+$ ground state. The $^2\Pi$ state is derivable from the $(4d)^9$ configuration of Rh and therefore it was expected that the error in the atomic limit would reveal itself through an upward shift of the $^2\Pi$ state relative to the $^2\Sigma^+$ ground state by $\sim$9000 cm^{-1}. Thus, the differences in atomic correlation energy of terms originating from different configurations play an entirely different role for this carbide molecule than for the transition metal dimers. This can probably be attributed to the delocalization of the Rh $4d$ orbitals that also indicate that the molecular orbital approximation is a good starting point for describing the RhC molecule.

C. Results of CI calculations of the RhC molecule

The molecular HF orbitals of the $^2\Sigma^+$ and the $^2\Pi$ states resemble each other considerably, and therefore it appears likely that a unique set of molecular orbitals could be derived for describing both states appropriately in CI calculations. In search for such molecular orbitals we performed CI calculations at the internuclear distance 3.05 a.u. using molecular orbitals optimized for a variety of states.

The CI calculations allowed full reorganization within the valence shells of the molecule ensuring a correct description of the molecule in the dissociation limit. The calcula-

TABLE III. Mulliken population analyses of the valence orbitals of the RhC molecule in the ground $^2\Sigma^+$ state and in the first excited $^2\Pi$ state. The calculations were performed in the HF approximation at the internuclear distance 3.05 a.u.

State	Orbital	Atomic population Rh	Atomic population C	Overlap population	Rh s	Rh p	Rh d	C s	C p	C d	Occupation number
$^2\Sigma^+$	10σ	0.43	1.51	0.06	0.03	0.02	0.41	1.50	0.04	0.00	2.00
	11σ	0.87	1.01	0.12	0.05	0.06	0.82	0.33	0.74	0.01	2.00
	12σ	0.68	0.29	0.03	0.58	0.01	0.10	−0.01	0.32	0.00	1.00
	5π	2.49	0.82	0.69	0.00	0.02	2.81	0.00	1.13	0.04	4.00
	2δ	4.00	0.00	0.00	0.00	0.00	4.00	0.00	0.00	0.00	4.00
Total		44.31	5.66	1.03	8.64	18.04	18.15	3.85	2.26	0.06	
$^2\Pi$	10σ	0.44	1.56	−0.02	0.02	0.01	0.41	1.54	0.03	0.00	2.00
	11σ	0.99	0.84	0.17	0.07	0.10	0.90	0.29	0.62	0.01	2.00
	5π	2.62	0.73	0.63	0.00	0.00	2.95	0.00	1.02	0.03	4.00
	6π	0.40	0.74	−0.07	0.00	0.09	0.23	0.00	0.67	0.00	1.00
	2δ	4.00	0.00	0.00	0.00	0.00	4.00	0.00	0.00	0.00	4.00
Total		44.31	5.91	0.77	8.08	18.13	18.49	3.87	2.38	0.05	

tions were carried out in the subgroup C_{2v} of the full symmetry group $C_{\infty v}$ of the RhC molecule. The number of configurations included within each symmetry species of C_{2v} reached 36 for the hextet states, 264 for the quartet states, and 484 for the doublet states.

The best result for the $^2\Sigma^+$ state was obtained using orbitals optimized for a mixture of a $^2\Pi$ and a $^2\Phi$ state,

FIG. 1. Potential energy curves for the RhC molecule of the $^2\Sigma^+$ ground state and of the first excited state, $^2\Pi$ as derived in HF (dashed lines) and CI (solid lines) calculations.

whereas the best results for the $^2\Pi$ state resulted from orbitals optimized for a mixture of the corresponding quartet states. In fact, the energy difference between the $^2\Sigma^+$ and the $^2\Pi$ states as derived from the optimal calculations is 9797 cm^{-1}. This is in very good agreement with the average of the experimentally determined T_e values, which are 9462.94 and 10 242.75 cm^{-1} for the $^2\Pi$ state.[8]

Finally, we decided to utilize the orbitals optimized for the mixture of the $^4\Pi$ and the $^4\Phi$ states for describing the low-lying electronic states of the RhC molecule. Of course, these orbitals do not provide the optimal description of the $^2\Sigma^+$ state, but they seem to be a reasonable choice as a unique set of molecular orbitals. The orbitals were optimized at the internuclear distances 2.90, 3.05, 3.30, 3.60, and 4.20 a.u. and utilized in CI calculations allowing full reorganization within the valence shells as described above.

In Fig. 1 we compare the potential energy curves of the $^2\Sigma^+$ and the $^2\Pi$ states derived in the HF approximation with those derived in the CI calculations. In the HF approximation the molecule is not described correctly in the dissociation limit. This, of course, is due to the ionic contributions in the wave functions which should vanish in the dissociation limit but cannot because of the delocalization of the molecular orbitals.

Table IV shows the Mulliken population analyses for the $^2\Sigma^+$ ground state as resulting from the CI calculations at the internuclear distance 3.05 a.u. The correlation included has resulted in a slight enhancement of the positive charge on the Rh atom, the gross atomic charge on Rh changes from $+0.17e$ in the HF calculations to $+0.24e$ in the CI calculations. This, however, is the final result of a substantial redistribution of charge caused by the inclusion of the correlation. Thus, in going from HF to CI 0.23 electron is transferred from the Rh $4d\pi$ orbital to the C $2p\pi$ orbital while 0.16 electron is transferred from the C $p\sigma$ orbital to the Rh $d\sigma$ and $s\sigma$ orbitals.

In both the HF and the CI description the major contributions to the overlap population are due to the 5π and the 11σ orbitals. The 12σ orbital, which contains 1.01 electron,
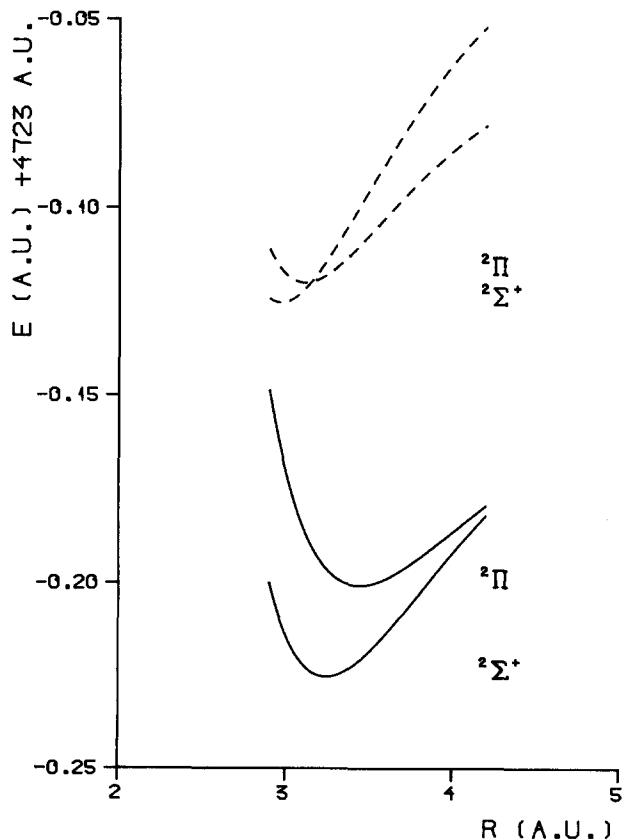
TABLE IV. Mulliken population analyses of the valence orbitals of the RhC molecule in the ground $^2\Sigma^+$ state as resulting from a CI treatment at the internuclear distance 3.05 a.u.

Orbital	Atomic population Rh	C	Overlap population	Orbital analysis Rh s	p	d	C s	p	d	Occupation number
10σ	0.90	1.03	0.06	0.00	0.00	0.94	0.82	0.23	0.01	2.00
11σ	0.51	1.33	0.14	0.10	0.09	0.38	1.00	0.39	0.01	1.98
12σ	0.71	0.31	− 0.01	0.61	0.01	0.08	− 0.01	0.32	0.00	1.01
5π	2.20	0.93	0.68	0.00	0.04	2.50	0.00	1.24	0.03	3.80
6π	0.11	0.14	− 0.03	0.00	0.02	0.07	0.00	0.13	0.00	0.22
2δ	3.99	0.00	0.00	0.00	0.00	3.99	0.00	0.00	0.00	3.99
Total	44.28	5.76	0.96	8.70	18.10	17.96	3.84	2.35	0.05	

does not contribute to the overlap population at all. The bond has triple bond character, a double bond originates from the combination of the $d\pi$ orbitals of Rh with the $p\pi$ orbitals of C. The third bond results mainly from combination of the Rh $d\sigma$ orbital and the $2s\sigma$ and $2p\sigma$ orbitals on C. While most charge in the π bonds is located on the Rh atom it is just the opposite in the σ bond. The bond may be interpreted in terms of donation and back-donation of charge. Thus, the population analyses of the nonbonding 12σ orbital (Table IV) indicate donation of charge from the $5s$ orbital of Rh into the $2p\sigma$ orbital of C. Back-donation occurs from the $2s$ orbital of C into mainly the $5p$ orbital of Rh. Altogether the bond between the Rh and the C atoms is polar with a total charge transfer of 0.24 electron from Rh to C. This gives rise to a dipole moment of 2.82 D for the $^2\Sigma^+$ ground state at the internuclear distance 3.05 a.u.

FIG. 2. Potential energy curves for the RhC molecule of the $^2\Sigma^+$ ground state and of 16 excited states as derived in CI calculations.

It is noted that the 6π orbitals in the $^2\Sigma^+$ ground state acquire a population of 0.22 electron in the CI calculations. This is presumably the reason for the much lower total energy derived in the CI calculations based on the molecular orbitals optimized for the mixture of the $^4\Pi$ and the $^4\Phi$ states rather than on those optimized for the $^2\Sigma^+$ state. The latter obviously leads to a relatively large population of the virtual 6π orbitals.

In Fig. 2 we present the potential energy curves for 17 electronic states of the RhC molecule. Regarding the potential energy curves exhibiting minima, we have fitted Morse functions to the calculated points of the potential energies. The equilibrium distances and the vibrational frequencies derived in the fitting process are reported in Table V. The dissociation energies reported in Table V are determined as differences between the energies of the RhC molecule at the equilibrium distances and the sum of the HF energies of the atoms. This procedure is consistent because the CI wave functions include only molecular correlation that vanish in the dissociation limit.

Several of the potential energy curves in Fig. 2 which appear to be repulsive have energies considerably lower than the sum of the energies of the separated atoms at the internu-
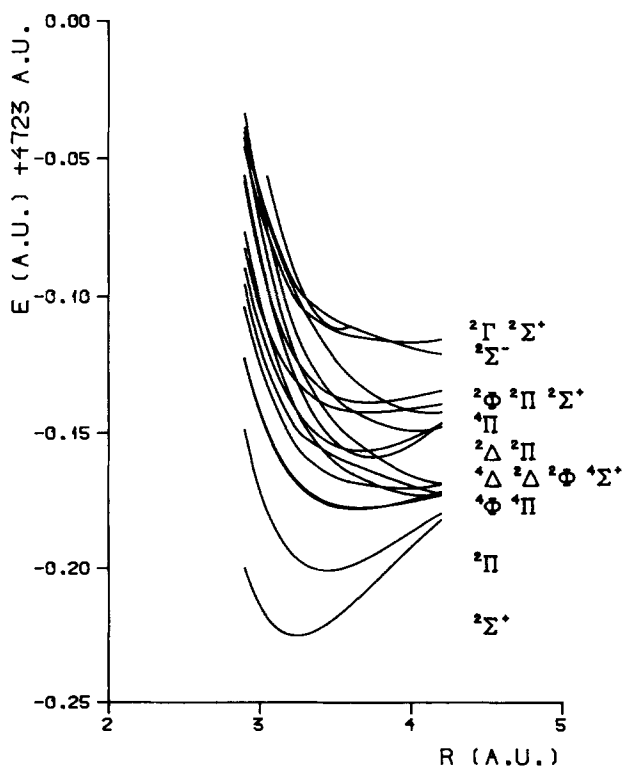
TABLE V. Spectroscopic constants for the low-lying electronic states of the RhC molecule as derived in HF and CI calculations. The states are listed in order of increasing energy at the internuclear distance 3.05 a.u.

State	Equilibrium distance (a.u.)	Dissociation energy (eV)	Vibrational frequency (cm^{-1})
$^2\Sigma^+$, HF	2.97	0.20	1026
$^2\Pi$, HF	3.11	0.06	850
$^2\Sigma^+$, CI	3.24	2.92	821
$^2\Pi$, CI	3.44	2.25	658
$^4\Phi$, CI	3.63	1.63	433
$^4\Pi$, CI	3.67	1.61	391
$^2\Phi$, CI	repulsive		
$^2\Delta$, CI	repulsive		
$^2\Pi$, CI	3.67	1.05	520
$^4\Delta$, CI	repulsive		
$^2\Phi$, CI	3.71	0.66	349
$^2\Pi$, CI	3.71	0.56	414
$^2\Delta$, CI	3.74	1.11	630
$^2\Sigma^+$, experimental	3.05[a]	5.97[b]	1049.87[a]
$^2\Pi$, experimental	3.13[a]		939.12,949.41[a]

[a] From Ref. 8.
[b] Present investigation.

clear distance 4.20 a.u. Therefore, these states probably have minima at internuclear distances larger than 4.20 a.u. indicating a considerable spread of equilibrium distances.

From Table V it is noted that the equilibrium distances and the vibrational frequencies derived for the $^2\Sigma^+$ and the $^2\Pi$ states in the HF approximation agree very well with the experimentally determined values. However, when CI is included the equilibrium distances are elongated, and the values derived from the CI calculations are ~ 0.2 a.u. larger than the experimental values. The CI calculations also cause the vibrational frequencies to reduce, and the final values of the vibrational frequencies for both the $^2\Sigma^+$ state and the $^2\Pi$ state are ~ 200 cm^{-1} below the experimental values. The changes in the spectroscopic constants in going from the HF to the CI approximation are due to inclusion of the left–right correlation required for a correct description of the molecule in the dissociation limit. Additional configurations should be included to improve the description of the molecule around the equilibrium distance, but this would require very large CI calculations that, most likely, would not change the description of the bonding significantly.

In addition, part of the discrepancy between the calculated and the experimental spectroscopic constants presumably can be attributed to the neglect of relativistic effects in the present work. Inclusion of relativistic effects would probably cause the equilibrium distances to decrease and the vibrational frequencies to increase thereby improving the agreement between the calculated and the experimental values.

The dissociation energy derived in our calculations for the $^2\Sigma^+$ ground state is only about half the experimental value, but this is according to our expectations with the amount of CI included. It is also in line with our earlier results on the Cu$_2$ molecule,[19] where we especially investigated the connection between the calculated dissociation energy and the amount of CI used. In the next section we present an experimental determination of the dissociation energy.

Table VI shows the population of the natural orbitals as functions of the internuclear distance for the $^2\Sigma^+$ ground state as well as for the first excited state, $^2\Pi$. As the dissociation limit is approached the populations of the 12σ and of the 6π orbitals are enhanced and those of the 11σ and the 5π are diminished for both states.

Figure 3 shows a deformation density map at the internuclear distance 3.05 a.u. It has been derived by subtracting the spherical averaged, superpositioned atomic charge densities from the charge density of the molecule in its $^2\Sigma^+$ ground state. The charge transfer from the Rh to the C atom is clearly recognized and the chemical bond also gives rise to an enhanced charge density halfway between the two nuclei.

III. MASS SPECTROMETRIC INVESTIGATION

The mass spectrometric equilibrium measurements involving gaseous RhC were performed with a single focusing, 12 in. radius magnetic-focusing-type instrument. The Ce–Rh–Ru–Os sample was mixed with excess graphite powder to insure unit activity of carbon during the measurements and placed into a graphite Knudsen cell. The graphite cell was inserted into a tantalum cell to avoid graphite losses at the highest temperatures of investigation. The orifice diameter was 0.040 in., and the combined channel length of the graphite and tantalum cell orifices was 0.020 in. The energy of the ionizing electrons was 20 V, the emission current was regulated at 1.0 mA. The ions were accelerated through a potential of 4.5 kV and detected with a 20 stage electron multiplier whose entrance shield was maintained at an ~ -2 kV potential. Temperatures were measured by sighting a Leeds and Northrup optical pyrometer at a blackbody hole at the bottom of the tantalum cell. The pyrometer had previously been calibrated *in situ* at the melting point of gold. The ionic species were identified by their mass to charge ratio m/e, isotopic abundance, and ionization efficiency.

TABLE VI. Occupations of the natural orbitals of the $^2\Sigma^+$ ground state and of the first excited state, $^2\Pi$ of RhC as functions of the internuclear distance.

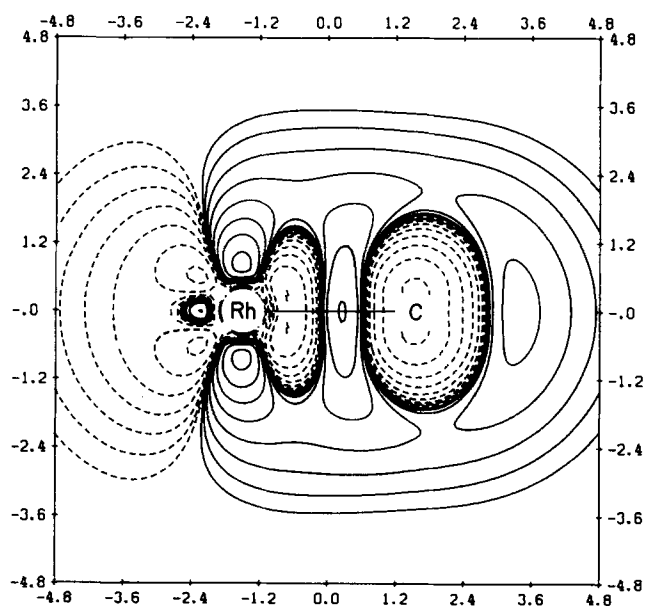| State	Orbital	Occupation				
		Distance (a.u.)				
		2.90	3.05	3.30	3.60	4.20
$^2\Sigma^+$	10σ	1.98	1.98	1.99	1.99	1.99
	11σ	2.00	2.00	1.96	1.93	1.91
	12σ	1.01	1.01	1.03	1.06	1.09
	5π	3.84	3.80	3.74	3.63	3.14
	6π	0.18	0.22	0.30	0.41	0.99
	2δ	3.99	3.99	3.99	3.98	3.88
$^2\Pi$	10σ	2.00	2.00	1.99	1.99	2.00
	11σ	1.97	1.95	1.91	1.84	1.57
	12σ	0.04	0.06	0.11	0.19	0.59
	5π	3.88	3.86	3.81	3.74	3.43
	6π	1.13	1.15	1.20	1.27	1.57
	2δ	3.98	3.98	3.98	3.97	3.84

FIG. 3. Deformation density map for the $^2\Sigma^+$ ground state of the RhC molecule at the internuclear distance 3.05 a.u. The superpositioned atomic charge densities from the $(4d)^8(5s)^1$ configuration of Rh and the $(2s)^2(2p)^2$ of C has been subtracted from the molecular charge density. Solid contours show enhanced electron charge relative to the superpositioned atoms, dashed contours show diminished charge. The smallest contour value is 0.000 625 e/a.u.^{3} Adjacent contours differ by a factor of 2.

TABLE VII. Third law enthalpies for the reaction Rh(g) + C(graph.) = RhC(g).

Data set number	T (K)	I(Rh$^+$)	I(RhC$^+$)	$-\log K_p$	$-\Delta[G_T^{\circ} - H_0^{\circ})/T]$ (J K^{-1})	ΔH_0° (kJ)
1	1970	2.790E-10	3.000E-12	1.9685	32.139	137.6
2	2012	5.190E-10	7.590E-12	1.8349	31.954	135.0
3	2045	7.780E-10	1.242E-11	1.7969	31.810	135.4
4	2088	1.230E-09	2.390E-11	1.7115	31.624	134.4
5	2088	1.170E-09	2.070E-11	1.7522	31.624	136.1
6	2140	1.870E-09	3.810E-11	1.6909	31.402	136.5
7	2177	2.700E-09	6.450E-11	1.6218	31.247	135.6
8	2177	2.700E-09	6.500E-11	1.6185	31.247	135.5
9	2212	3.880E-09	1.035E-10	1.5739	31.102	135.5
10	2212	4.000E-09	1.050E-10	1.5809	31.102	135.7
11	2248	5.950E-09	1.770E-10	1.5265	30.954	135.3
12	2248	5.900E-09	1.720E-10	1.5353	30.954	135.7
13	2280	8.100E-09	2.514E-10	1.5081	30.824	136.1
14	2280	8.000E-09	2.430E-10	1.5175	30.824	136.5
15	2319	1.119E-08	3.640E-10	1.4877	30.667	137.2
16	2319	1.086E-08	3.300E-10	1.5173	30.667	138.5
17	2223	2.730E-09	6.800E-11	1.6037	31.056	137.3
18	2191	2.010E-09	4.880E-11	1.6148	31.189	136.1
19	2191	1.980E-09	4.680E-11	1.6264	31.189	136.6
20	2161	1.400E-09	3.000E-11	1.6690	31.314	136.7
21	2126	9.650E-10	1.950E-11	1.6945	31.462	135.9
22	2104	7.340E-10	1.425E-11	1.7119	31.555	135.3
23	2076	4.950E-10	8.400E-12	1.7703	31.675	136.1
24	2054	3.450E-10	5.100E-12	1.8302	31.770	137.2
25	2235	2.900E-09	7.500E-11	1.5873	31.007	137.2
26	2264	3.430E-09	9.300E-11	1.5668	30.889	137.8
27	2293	5.160E-09	1.410E-10	1.5634	30.771	139.2
28	2318	6.720E-09	1.938E-10	1.5400	30.671	139.4
29	2340	9.300E-09	2.700E-10	1.5371	30.584	140.4
34	2330	5.900E-09	1.875E-10	1.4979	30.624	138.2
35	2276	3.350E-09	9.420E-11	1.5510	30.840	137.8
36	2242	2.136E-09	5.500E-11	1.5892	30.978	137.7
37	2217	1.710E-09	4.250E-11	1.6046	31.081	137.0
38	2202	1.350E-09	3.210E-11	1.6238	31.143	137.0
39	2194	1.101E-09	2.500E-11	1.6438	31.176	137.4
40	2164	8.750E-10	1.810E-11	1.6843	31.301	137.5
41	2151	6.940E-10	1.400E-11	1.6952	31.356	137.3
42	2139	5.650E-10	1.125E-11	1.7009	31.407	136.8
43	2107	4.150E-10	7.500E-12	1.7430	31.543	136.8
44	2086	2.775E-10	4.600E-12	1.7805	31.632	137.1
47	2443	1.875E-08	6.860E-10	1.4367	30.184	140.9
48	2443	1.440E-08	5.450E-10	1.4220	30.184	140.3
49	2273	2.130E-09	6.150E-11	1.5395	30.852	137.1
50	2273	2.270E-09	6.150E-11	1.5672	30.852	138.3
51	2427	1.254E-08	4.800E-10	1.4171	30.245	139.2
52	2448	1.425E-08	5.900E-10	1.3830	30.165	138.7
53	2518	2.610E-08	1.239E-09	1.3236	29.903	139.1
54	2576	2.832E-08	1.725E-09	1.2153	29.691	136.4
55	2576	3.720E-08	2.070E-09	1.2546	29.691	138.4
56	2484	1.440E-08	6.500E-10	1.3454	30.029	138.6
57	2266	1.380E-09	3.650E-11	1.5776	30.880	138.4
58	2253	1.275E-09	3.350E-11	1.5805	30.933	137.9
59	2279	1.665E-09	4.720E-11	1.5475	30.828	137.8
60	2307	2.310E-09	7.050E-11	1.5154	30.715	137.8
61	2356	3.750E-09	1.320E-10	1.4535	30.521	137.5
62	2225	8.300E-10	2.000E-11	1.6180	31.048	138.0
63	2191	5.050E-10	1.020E-11	1.6947	31.189	139.4
64	2411	6.350E-09	2.610E-10	1.3861	30.307	137.1
65	2446	9.400E-09	3.930E-10	1.3787	30.173	138.4
66	2459	1.020E-08	4.480E-10	1.3573	30.123	138.0
67	2491	1.518E-08	7.000E-10	1.3362	30.003	138.5
68	2553	2.553E-08	1.368E-09	1.2710	29.774	138.1
69	2553	2.850E-08	1.485E-09	1.2831	29.774	138.7
70	2589	4.392E-08	2.580E-09	1.2310	29.644	137.8
74	2609	5.910E-08	3.700E-09	1.2034	29.573	137.3
75	2631	6.103E-08	3.950E-09	1.1889	29.495	137.5
76	2631	5.860E-08	3.810E-09	1.1870	29.495	137.4
77	2168	4.610E-10	1.050E-11	1.6425	31.285	136.0

TABLE VII. (continued).

Data set number	T(K)	I(Rh$^+$)	I(RhC$^+$)	$-\log K_p$	$-\Delta\,[G^{\cdot}_T - H^{\cdot}_0)/T]$ (J K^{-1})	$\Delta H^{\cdot}_0$ (kJ)
78	2362	4.620E-09	1.593E-10	1.4624	30.497	138.2
79	2353	4.780E-09	1.750E-10	1.4364	30.533	136.6
80	2325	3.800E-09	1.284E-10	1.4712	30.643	136.7
81	2371	5.870E-09	2.265E-10	1.4136	30.462	136.4
82	2403	8.300E-09	3.300E-10	1.4006	30.338	137.3
83	2435	8.620E-09	3.750E-10	1.3615	30.215	137.0
84	2461	1.185E-08	5.600E-10	1.3255	30.116	136.6
85	2496	1.794E-08	8.880E-10	1.3054	29.984	137.2
86	2525	2.403E-08	1.275E-09	1.2752	29.877	137.1
87	2558	3.012E-08	1.830E-09	1.2164	29.756	135.7
88	2585	3.300E-08	2.010E-09	1.2153	29.659	136.8
89	2732	3.710E-08	2.840E-09	1.1161	29.147	138.0
90	2770	2.400E-08	2.160E-09	1.0458	29.021	135.8
91	2734	1.030E-08	9.300E-10	1.0444	29.141	134.3
92	2769	1.410E-08	1.050E-09	1.1280	29.024	140.2
93	2784	3.730E-09	3.130E-10	1.0762	28.975	138.0
94	2806	9.000E-10	9.300E-11	0.9858	28.903	134.1

Average $\Delta H^{\cdot}_0 = 137.1 \pm 1.2$

The determination of the dissociation energy of RhC was based on the equilibrium reaction

$$\text{Rh(g)} + \text{C(graphite)} = \text{RhC(g)} \qquad (1)$$
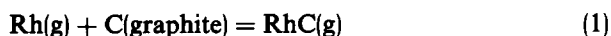
which is independent of the absolute pressure calibration of the instrument. The measured relative ion currents of Rh$^+$ and RhC$^+$ were assumed proportional to the corresponding partial pressures and used in deriving the reaction enthalpy, ΔH, by the second law:

$$\Delta H^{\cdot}_T = -R\,[d \ln K_p/d\,(1/T)]$$

as well as by the third law:

$$\Delta H^{\cdot}_\theta = -RT \ln K_p(T) - T[G^{\cdot}_T - H^{\cdot}_\theta/T].$$

In the evaluation of the equilibrium constant K_p from the relative ion currents it was assumed that the effective relative ionization cross sections and multiplier gains of Rh$^+$ and RhC$^+$ cancel each other. The thermodynamic functions for Rh(g) and C(graphite) were taken from Hultgren et al.,[20] and those for RhC(g) from Cocke and Gingerich.[7(a)] The thermal functions for RhC have been based on experimental, molecular constants determined by Scullman and associates.[3,4] This choice is appropriate, since our theoretical calculations did not reveal any additional low lying electronic states. The log K_p values and Gibbs energy function changes, $-\Delta\,(G^{\cdot}_T - H^{\cdot}_0)/T]$ for reaction (1) as well as the resulting third law $\Delta H^{\cdot}_0$ values are given in Table VII. The average third law values are: $\Delta H^{\cdot}_0 = 137.3 \pm 1.3$ kJ mol^{-1} or 32.8 ± 0.3 kcal mol^{-1} and $\Delta H^{\cdot}_{298} = 138.8 \pm 1.3$ kJ mol^{-1} or 33.2 ± 0.03 kcal mol^{-1}. The corresponding second law values are: $\Delta H^{\cdot}_{2315} = 110.6 \pm 1.7$ kJ mol^{-1} or 26.2 ± 0.4 kcal mol^{-1}, $\Delta H^{\cdot}_0 = 132.2 \pm 1.7$ kJ mol^{-1} or 31.6 ± 0.4 kcal mol^{-1}, and $\Delta H^{\cdot}_{298} = 133.7 \pm 1.7$ kJ mol^{-1} or 32.0 ± 0.4 kcal mol^{-1}. Here the error terms represent standard deviations.

We select the average of the second and third law enthalpies: $\Delta H^{\cdot}_0 = 134.8 \pm 3.4$ kJ mol^{-1} or 32.2 ± 0.8 kcal mol^{-1}. The corresponding $\Delta H^{\cdot}_{298}$ value is 136.3 ± 3.4 kJ mol^{-1} or 32.6 ± 0.8 kcal mol^{-1}. Together with the heat of sublimation of graphite, $\Delta H^{\cdot}_{f,0}$ [C(g)] of 169.6 ± 0.5 kcal mol^{-1} [20] a dissociation energy of RhC(g), $D^{\cdot}_0 = 137.4 \pm 1.0$ kcal mol^{-1} (574.9 ± 4.2 kJ mol^{-1}) results.

Our present results are compared in Table VIII with the corresponding literature values obtained for reaction (1). It is noted that there is very good agreement between our present results and the literature data. Cocke and Gingerich[7] have evaluated additional equilibrium reactions and arrived at a selected dissociation energy $D^{\cdot}_0$(RhC) = 138.5 ± 2.0 kcal mol^{-1}. Small differences in the third law results are due to slightly different values in the thermal functions used by Vander Auwera-Mahieu and Drowart[6] on one hand and by Cocke and Gingerich[7] and in the present investigation on the other hand. Another small difference stems from alternate evaluations of the equilibrium constants for reaction (1). We have here adopted the simplifying assumptions used by Vander Auwera-Mahieu, whereas Cocke and Gingerich have taken estimated ionization cross sections and measured multiplier gains into account. The much larger number of measured data points and temperature range covered in the present investigation is particularly reflected in the very small standard deviation for the second-law reaction enthalpy. The current investigation of gaseous RhC demonstrates that under favorable experimental conditions and when the molecular parameters of the molecule under investigation are known, the dissociation energy of the diatomic molecule may be determined with high accuracy by Knudsen effusion mass spectrometry. Considering the present results and the literature data we select 576.0 ± 3.8 kJ mol^{-1} or 137.7 ± 0.9 kcal mol^{-1} for the dissociation energy $D^{\cdot}_0$ of RhC(g).

TABLE VIII. Comparison of the reaction enthalpies for $Rh(g) + C(graph.) = RhC(g)$ and derived dissociation energies of $RhC(g)$ (in kcal mol^{-1}).

Temperature range (K)	No of data sets	ΔH°_0(2nd law)	ΔH°_0(3rd law)	ΔH°_0(selected)	D°_0(RhC)[a]	Ref.
2095–2365	17	30.3 ± 1.7[b]	31.1 ± 1.5[c]	31.1 ± 1.5	138.5 ± 1.5	6
1920–2536	25	29.2 ± 0.6[b]	33.6 ± 0.4[b]	31.4 ± 2.0	138.2 ± 2.0	7(a)
1970–2806	85	31.6 ± 0.4[b]	32.8 ± 0.3[b]	32.2 ± 0.8	137.4 ± 1.0	

[a] Using $\Delta H^{\circ}_{f,0}$ [C(g)] = 169.6 ± 0.5 kcal mol^{-1}, Ref. 20.
[b] Error term corresponds to the standard deviation.
[c] Error includes also the term caused by the assumptions used in calculating K_p.

IV. CONCLUSIONS

In the present work we have reported results of both theoretical and experimental investigations of the RhC molecule. The electronic structure of the molecule has been elucidated through all-electron *ab initio* HF-CI calculations as functions of the internuclear distance, and the dissociation energy has been determined from mass spectrometric equilibrium measurements.

The calculational results for the $^2\Sigma^+$ ground state and also for the first excited state, $^2\Pi$, are in good agreement with experimental data. The small differences between the calculated and the experimental spectroscopic constants can be explained by the neglect of the relativistic effects.

The chemical bond between the Rh and the C atoms is a triple bond composed of two π bonds and one σ bond. The bonding orbitals can be characterized as combinations of the $d\sigma$ and the $d\pi$ orbitals of Rh with the $s\sigma$ and $p\sigma$ orbitals of C. The $5s$ orbital of Rh hardly participates in the bonding, but it is part of a singly occupied, nonbonding orbital from which a charge donation to the $2p\sigma$ orbital of C occurs. The bond in the RhC molecule is polar with a total charge transfer of 0.24 electron from Rh to C. This results in a dipole moment of 2.82 D in the $^2\Sigma^+$ ground state.

The triple bond nature of the chemical bond in the RhC molecule revealed in our calculations is in good agreement with the very high value of the dissociation energy determined in our mass spectrometric measurements. Considering the results of the present investigation in conjunction with the literature data we have selected 576.0 ± 3.8 kJ mol^{-1} as the dissociation energy D°_0 of RhC(g).

ACKNOWLEDGMENTS

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