Eur. Phys. J. D **7**, 163–172 (1999)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences

All electron ab initio investigations of the electronic states of the FeC molecule

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Received: 2 October 1998 / Received in final form: 30 March 1999

Abstract. The low-lying electronic states of the molecule FeC have been investigated by performing all electron *ab initio* multi-configuration self-consistent-field (CASSCF) and multi reference configuration interaction (MRCI) calculations. The relativistic corrections for the one-electron Darwin contact term and the relativistic mass-velocity correction have been determined in perturbation calculations. The electronic structure of the FeC molecule is interpreted as antiferromagnetic couplings of the localized angular momenta of the ions Fe^+ and C^- resulting in a triple bond in the valence bond sense. The electronic ground state is confirmed as being $^3\Delta$. The spectroscopic constants for the ground state and eleven excited states have been derived from the results of the MRCI calculations. The spectroscopic constants for the $^3\Delta$ ground state have been determined as $r_e = 1.585$ Å and $\omega_e = 859$ cm^{-1}, and for the low-lying $^1\Delta$ state as $r_e = 1.567$ Å and $\omega_e = 962$ cm^{-1}. The values for the ground state agree well with the available experimental data. The FeC molecule is polar with charge transfer from Fe to C. The dipole moment has been determined as 1.86 D in the $^3\Delta$ ground state and as 1.51 D in the $^1\Delta$ state. From the results of the MRCI calculations the dissociation energy, D_e, is determined as 2.79 eV, and D_0 as 2.74 eV.

PACS. 31.25.Nj Electron-correlation calculations for diatomic molecules – 31.50.+w Excited states – 33.15.-e Properties of molecules and molecular ions

1 Introduction

With the present investigation of the FeC molecule we are continuing our systematic study of the electronic structure and nature of bonding in diatomic transition metal carbides [1–10]. Apart for our early work on the molecules CoC and NiC [5,6], the present work represents the first thorough *ab initio* study of the low-lying electronic states of an iron group carbide molecule.

Recently several research groups have investigated the FeC molecule in the gas phase. Balfour *et al.* [11] have measured several electronic states of FeC by electron spectroscopy. Their work has established the electronic ground state of FeC as $^3\Delta$, and also the existence of a low-lying $^1\Delta$ excited state. The mean internuclear distance, r_0, was reported as 1.596 Å for $^3\Delta_3$, 1.591 Å for $^3\Delta_2$, and as 1.595 Å for the low-lying excited state, $^1\Delta$. Furthermore, Allen *et al.* [12] have measured the pure rotational spectrum of FeC. The rotational constant of FeC has been determined to high precision in Allen *et al.*'s work, but basically the results are in agreement with those obtained by Balfour *et al.* [11]. Brugh and Morse [13] have used resonant two-photon ionization spectroscopy to investigate the electronic states located 12000 to 18100 cm^{-1} above the ground state. Their work has confirmed that the ground state is $^3\Delta$. In addition, they have identified six new electronic states.

In the present investigation we have carried out all electron *ab initio* calculations to determine the low-lying electronic states of FeC. The methods employed are multi-configuration self-consistent-field (MCSCF) calculations within the complete active space self-consistent-field approach (CASSCF). In addition, several of the low-lying states have been investigated by performing multi reference configuration interaction (MRCI) calculations. The relativistic effects on the low-lying electronic states have been considered by performing perturbation calculations of the one-electron Darwin contact term and also of the relativistic mass-velocity term. The calculations have been carried out using the program system MOLCAS, version 3 [14].

2 Basis sets

The basis sets consisted of contracted Gaussian-type functions. For the Fe atom we have used Wachters' (14*s*, 9*p*, 5*d*) basis set [15], but it has been extended by addition of two *p* functions with exponents 0.2019 and 0.0821. These functions are needed to represent the 4*p* orbitals.

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In addition, the most diffuse s functions have been contracted slightly by altering the exponents from 0.114220 and 0.041889 to 0.2019 and 0.0672, respectively. Finally an f polarization function with exponent 1.696 was added. The primitive basis set ($14s$, $11p$, $5d$, $1f$) was contracted to ($8s$, $6p$, $3d$, $1f$) using a segmented contraction scheme. In the contracted basis the $3d$ orbital is represented by a triple zeta function while all other orbitals including the unoccupied $4p$ orbital are represented by double zeta functions. For the C atom we have used Huzinaga's ($10s$, $6p$) basis [16], but it has been augmented by a d polarization function with exponent 0.75. The basis set for the C atom was contracted to ($4s$, $3p$, $1d$) resulting in double zeta representation of the s functions, triple zeta representation of the $2p$ function, and a d polarization function.

3 Results of CASSCF calculations on the FeC molecule

Our previous work on the NiC molecule [5,6] has shown that this molecule has many low-lying electronic states that can be rationalized as arising from coupling of the angular momenta of the ions ${}^4F_g\mathrm{Ni}^+$ and ${}^4S_u\mathrm{C}^-$. Similar trends are expected for the FeC molecule. Coupling of the angular momenta of ${}^6D_g\mathrm{Fe}^+$ and ${}^4S_u\mathrm{C}^-$ gives rise to triplet, quintet, septet and nonet states of the symmetries Σ^-, Π, and Δ. CASSCF calculations have been performed for singlet, triplet, quintet, septet and nonet states.

In the CASSCF calculations the core orbitals, *i.e.* $1s$, $2s$, $3s$, $2p$, and $3p$, of Fe and $1s$ of C, were kept fully occupied, while the valence orbitals $4s$ and $3d$ of Fe and $2s$ and $2p$ of C have been included in the active space. The CASSCF calculations have been performed in the subgroup C_{2v} of the full symmetry group $C_{\infty v}$ of the FeC molecule. The number of configurations included in the CASSCF calculations reached 3440 for the singlet states, 5220 for the triplet states, 2070 for the quintet states, 292 for the septet states, and 12 for the nonet states.

The influence of the relativistic effects have been determined by carrying out perturbation calculations to derive values for the one-electron Darwin contact term and for the relativistic correction due to the mass-velocity term.

The CASSCF calculations have been performed as functions of the internuclear distance, *i.e.* for the distances 3.0, 3.15, 3.3, 3.6, 3.9, 4.2, 4.5, 5.0, 7.0, and 12.0 a.u. For the states ${}^1\Pi$, ${}^3\Sigma^-$, and ${}^5\Pi$ calculations have also been performed for the internuclear distance 2.85 a.u., and for the ${}^3\Delta$ ground state and the ${}^1\Delta$ excited state at 2.85 and 2.70 a.u. The resulting potential energy curves shown in Figure 1 are based on potential energies that include the relativistic corrections. Table 1 presents the spectroscopic constants obtained by solving the Schrödinger equation for the nuclear motion numerically using the potential energies derived in the CASSCF calculations excluding and including the relativistic corrections. The dissociation energies included in Table 1 have been derived by subtracting the total energy at the equilibrium distance from the total energy of each state at 12 a.u., where available.

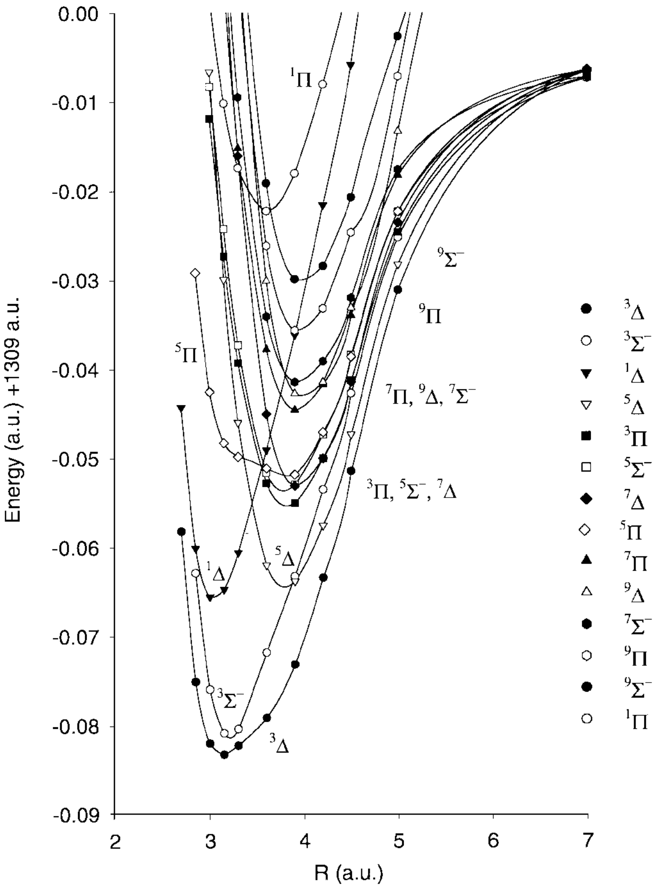

Fig. 1. Potential energy curves of 14 low-lying electronic states of the FeC molecule as derived from CASSCF calculations including the relativistic corrections for the one-electron Darwin contact term and for the mass-velocity term.

From Figure 1 and Table 1 it is recognized that the electronic ground state of the FeC molecule is ${}^3\Delta$ in agreement with the recent spectroscopic work by Balfour *et al.* [11] and Brugh *et al.* [13]. Including the relativistic corrections, the ${}^3\Delta$ ground state is separated from the higher-lying states, ${}^3\Sigma^-$, ${}^1\Delta$, ${}^5\Delta$, ${}^3\Pi$, ${}^5\Sigma^-$, ${}^7\Delta$, ${}^5\Pi$, ${}^7\Pi$, ${}^9\Delta$, ${}^7\Sigma^-$, ${}^9\Pi$, ${}^9\Sigma^-$, and ${}^1\Pi$ by the transition energies 468, 3843, 4143, 6128, 6511, 6599, 6847, 8482, 8736, 9154, 10398, 11592, and 13384 cm^{-1}, respectively. From Table 1 it is recognized that the relativistic correction is largest for the ${}^3\Sigma^-$ state which has the largest occupation of the Fe $4s$ orbital. Thus, the relativistic corrections cause the energy separation between the ${}^3\Delta$ ground state and the ${}^3\Sigma^-$ lowest-lying excited state to decrease from 1923 to 468 cm^{-1}. Furthermore, the relativistic corrections cause the state ${}^5\Sigma^-$ to drop below the states ${}^7\Delta$ and ${}^5\Pi$.

All the triplet, quintet, and septet states investigated are dissociating to ground term atoms whereas the singlet and nonet states are dissociating to excited terms of the Fe atom. On basis of the results of the CASSCF calculations without relativistic corrections, the dissociation energy, D_e, of the ${}^3\Delta$ ground state of FeC has been derived as 2.17 eV. When the relativistic corrections are included the value of D_e is reduced to 2.10 eV. Furthermore,

Table 1. Spectroscopic constants of the low-lying electronic states of the FeC molecule as derived from the results of CASSCF calculations. Also included is the population of the Fe 4s orbital at 3.15 a.u.

State	Excluding relativistic corrections					Including relativistic corrections			
	Equilibrium distance r_e (Å)	Vibrational frequency $\omega_\mathrm{e}(\mathrm{cm}^{-1})$	Transition energy $T_\mathrm{e}(\mathrm{cm}^{-1})$	Dissociation energy[a] D_e(eV)	Population of Fe 4s at 3.15 a.u.	Equilibrium distance r_e (Å)	Vibrational frequency $\omega_\mathrm{e}(\mathrm{cm}^{-1})$	Transition energy $T_\mathrm{e}(\mathrm{cm}^{-1})$	Dissociation energy[a], D_e(eV)
$^3\Delta$	1.659	557	0	2.17	0.80	1.658	546	0	2.10
$^3\Sigma^-$	1.713	671	1923	1.92	1.32	1.697	707	468	2.02
$^1\Delta$	1.618	744	3554	4.49	0.91	1.611	761	3843	4.36
$^5\Delta$	2.013	543	4169	1.66	0.80	2.008	544	4143	1.59
$^3\Pi$	2.027	498	6231	1.40	0.79	2.021	499	6128	1.34
$^5\Sigma^-$	2.018	510	7003	1.29	0.88	2.002	519	6511	1.28
$^7\Delta$	2.087	548	6582	1.36	0.81	2.083	547	6599	1.28
$^5\Pi$	2.031	416	6964	1.31	0.80	2.022	399	6847	1.25
$^7\Pi$	2.088	514	8558	1.11	0.82	2.082	515	8482	1.05
$^9\Delta$	2.125	573	8648	2.92	0.83	2.119	575	8736	2.91
$^7\Sigma^-$	2.100	497	9429	0.99	0.91	2.090	500	9154	0.95
$^9\Pi$	2.103	554	10364	3.09	0.84	2.095	558	10398	3.09
$^9\Sigma^-$	2.125	540	11644	2.93	0.94	2.114	543	11592	
2 $^3\Delta$	1.909	483	11959						
$^1\Pi$	1.910	520	13013	3.32	0.95	1.901	525	13384	3.18

[a] Derived as the difference between the total molecular energy at the equilibrium distance and at the internuclear distance 12 a.u. for each state. The effect of basis set superposition errors reduce the values by 0.04 eV.

Table 2. The contributions of the major configurations to the CASSCF wave functions describing the $^3\Delta$ ground state and the low-lying excited states of the FeC molecule as functions of the internuclear distance.

State	Valence shell configuration							Contribution of valence shell configuration (%)						
	7σ	8σ	9σ	10σ	3π	4π	1δ	Internuclear distance (a.u.)						
	(C s)	(σ)	(Fe σ)	(σ^*)	(π)	(π^*)		2.7	2.85	3.0	3.15	3.3	3.6	3.9
$^3\Delta$	2	2	1	0	4	0	3	81	76	70	61	50	28	18
$^3\Sigma^-$	2	2	2	0	4	0	2		74	69	63	56	37	22
$^1\Delta$	2	2	1	0	4	0	3	80	76	70	62	53	34	22
$^5\Delta$	2	2	1	0	3	1	3			62	50	41	32	28
	2	1	1	1	4	0	3			9	12	12	10	7
$^3\Pi$	2	2	1	0	4	1	2			54	53	51	34	32
$^7\Delta$	2	1	1	1	3	1	3			52	48	45	37	31
	2	2	1	0	2	2	3			25	24	24	36	30
$^5\Pi$	2	2	1	0	4	1	2		80	76	70	62	34	22
$^5\Sigma^-$	2	2	1	1	4	0	2			64	47	20	8	6
	2	2	2	0	3	1	2			3	12	32	37	35
$^7\Pi$	2	2	1	0	3	2	2			80	52	38	36	
$^9\Delta$	2	1	1	1	2	2	3				100	100	100	100
$^7\Sigma^-$	2	2	1	1	3	1	2			69	61	52	37	27
	2	2	2	0	2	2	2			7	11	17	30	40
$^9\Pi$	2	1	1	1	3	2	2				100	100	100	100
$^9\Sigma^-$	2	2	1	1	2	2	2				100	100	100	100
$^1\Pi$	2	2	1	0	4	1	2		75	69	62	54	40	30

Table 3. Occupations in the natural orbitals for the low-lying electronic states of FeC as derived in CASSCF calculations. Also included are the dipole moments at the respective internuclear distances.

State	Internuclear distance (a.u.)	Dipole moment (D)	Population in						
			7σ (C s)	8σ (σ)	9σ (Fe σ)	10σ (σ^*)	3π (π)	4π (π^*)	1δ
$^3\Delta$	3.00	1.660	1.99	1.83	1.01	0.16	3.56	0.45	2.99
$^3\Sigma^-$	3.15	1.842	1.99	1.86	1.98	0.16	3.47	0.54	2.01
$^1\Delta$	3.00	1.400	1.99	1.83	1.01	0.17	3.56	0.45	2.99
$^5\Delta$	3.60	2.092	2.00	1.38	1.00	0.62	2.50	1.50	3.00
$^3\Pi$	3.60	2.762	2.00	1.52	1.00	0.48	3.40	1.60	2.00
$^7\Delta$	3.90	2.599	2.00	1.22	1.00	0.78	2.16	1.84	3.00
$^5\Pi$	3.15	2.584	1.99	1.77	1.01	0.22	3.67	1.33	2.01
$^5\Sigma^-$	3.60	2.297	2.00	1.49	1.98	0.53	2.51	1.50	2.00
$^7\Pi$	3.90	2.994	2.00	1.31	1.00	0.69	3.08	1.93	2.00
$^9\Delta$	3.90	2.303	2.00	1.00	1.00	1.00	2.00	2.00	3.00
$^7\Sigma^-$	3.90	2.808	2.00	1.31	1.99	0.69	2.15	1.85	2.00
$^9\Pi$	3.90	2.502	2.00	1.00	1.00	1.00	3.00	2.00	2.00
$^9\Sigma^-$	3.90	2.557	2.00	1.00	2.00	1.00	2.00	2.00	2.00
$^1\Pi$	3.15	2.234	1.99	1.72	1.01	0.27	3.63	1.37	2.02

investigations of basis set superposition errors show that the above values are both reduced by 0.04 eV when basis set superposition errors are included.

4 The low-lying electronic states of the FeC molecule

Table 2 shows the major configurations in the CASSCF wave functions for the electronic ground state, $^3\Delta$, and for the low-lying excited electronic states as functions of the internuclear distance. Table 3 reports the occupations of the natural valence orbitals for all the low-lying states at internuclear distances close to the equilibrium distance of each state as derived from the results of the MRCI calculations discussed below. Also included are the dipole moments at the respective internuclear distances, but it should be realized that the dipole moments vary considerably with the internuclear distance. Results of population analysis for the low-lying electronic states are shown in Table 4.

The valence orbitals of FeC can be characterized as follows: the 7σ orbital is basically the C $2s$ orbital. The 8σ orbital is the bonding combination of the C $2p\sigma$ and the Fe $3d\sigma$, and the 10σ orbital is the corresponding antibonding orbital. The orbital 9σ is mainly a non-bonding hybrid orbital localized on Fe and polarized to remove charge from the internuclear region. The 3π orbital is the bonding combination of the C $2p\pi$ and the Fe $3d\pi$. The 4π orbital is the corresponding antibonding orbital. From Table 3 it is noted that the 7σ orbital is practically fully occupied in all the low-lying states.

Table 2 reveals that the contributions of the major configurations are surprisingly small, even at internuclear distances close to the equilibrium distance of the molecule. Thus, the major configuration of the $^3\Delta$ ground state at 3.00 a.u., $(7\sigma)^2(8\sigma)^2(9\sigma)^1(3\pi)^4(1\delta)^3$, only contributes with 70%. Similar trends are found for the low-lying excited states. The bond order of the leading configuration of the ground state is three due to occupation of the bonding orbitals 8σ and 3π, but if the results of Table 3 are used the approximate bond order in the $^3\Delta$ ground state is only 2.36 due to the occupancy of the antibonding orbitals, 10σ and 4π.

Since the $^3\Delta$ ground state and the low-lying $^1\Delta$ excited state both have the major configuration $(7\sigma)^2(8\sigma)^2(9\sigma)^1$ $(3\pi)^4$ $(1\delta)^3$, these states basically represent triplet and singlet exchange coupling between electrons in the molecular orbitals 9σ and 1δ. In accordance with the low weights of the major configuration for the states, $^3\Delta$ and $^1\Delta$, Table 3 shows that the antibonding 4π orbitals acquire significant population amounting to $0.45e$ for both $^3\Delta$ and $^1\Delta$ at 3.00 a.u. The populations of the antibonding orbital 10σ amount to $0.16e$ in $^3\Delta$ and of $0.17e$ in $^1\Delta$ at 3.00 a.u. Table 4 shows that the occupation of the $3d$ shell of Fe at 3.00 a.u. amounts to $6.60e$ for the $^3\Delta$ ground state and to $6.61e$ for the low-lying $^1\Delta$ excited state. Thus, these states arise from mixtures of configurations with six, respectively, seven $3d$ electrons on Fe. The major configurations of the remaining states of Δ symmetry are: $(7\sigma)^2(8\sigma)^2(9\sigma)^1(3\pi)^3(4\pi)^1(1\delta)^3$ for $^5\Delta$, $(7\sigma)^2(8\sigma)^1(9\sigma)^1(10\sigma)^1(3\pi)^3(4\pi)^1(1\delta)^3$ for $^7\Delta$, and $(7\sigma)^2(8\sigma)^1(9\sigma)^1(10\sigma)^1(3\pi)^2(4\pi)^2(1\delta)^3$ for $^9\Delta$. At 3.15 a.u. the contribution of the major configuration for the $^5\Delta$ state is 50%, for the $^7\Delta$ state it is 48%, but for $^9\Delta$ it is 100%.

The low-lying excited $^3\Sigma^-$ state has the major configuration $(7\sigma)^2(8\sigma)^2(9\sigma)^2(3\pi)^4(1\delta)^2$, which contributes 63% to the wave function at 3.15 a.u. This state can be considered as arising from the $^3\Delta$ ground state by transfer of one electron from the 1δ to the 9σ orbital. Since the $^3\Sigma^-$ state is separated from the $^3\Delta$ ground state by only 468 cm^{-1},

Table 4. Results of population analysis for the low-lying electronic states of FeC based on the results of the CASSCF calculations. Also shown are the gross atomic charge and the total number of *d* electrons on Fe.

State	Internuclear distance (a.u.)	Gross atomic charge on Fe	Number of *d* electrons on Fe	Population								
				Fe						C		
				$3d\sigma$	$3d\pi$	$3d\delta$	$4s$	$4p\sigma$	$4p\pi$	$2s$	$2p\sigma$	$2p\pi$
$^3\Delta$	3.00	0.29	6.60	1.24	2.37	2.99	0.80	0.25	0.07	1.85	0.85	1.56
$^3\Sigma^-$	3.15	0.28	6.17	1.54	2.62	2.01	1.32	0.17	0.07	1.86	1.09	1.31
$^1\Delta$	3.00	0.22	6.61	1.28	2.33	2.99	0.90	0.20	0.07	1.82	0.79	1.59
$^5\Delta$	3.60	0.53	6.19	1.07	2.12	3.00	0.85	0.36	0.07	1.80	0.92	1.81
$^3\Pi$	3.60	0.53	6.16	1.07	3.12	2.00	0.87	0.34	0.07	1.81	0.91	1.81
$^7\Delta$	3.90	0.56	6.09	1.04	2.05	3.00	0.89	0.38	0.07	1.78	0.91	1.88
$^5\Pi$	3.15	0.40	6.34	1.30	3.04	2.01	0.80	0.27	0.19	1.82	0.80	1.76
$^5\Sigma^-$	3.60	0.49	6.05	1.89	2.16	2.00	1.04	0.33	0.08	1.81	0.91	1.76
$^7\Pi$	3.90	0.55	6.07	1.04	3.03	2.00	0.93	0.35	0.08	1.79	0.88	1.88
$^9\Delta$	3.90	0.56	6.05	1.03	2.02	3.00	0.88	0.42	0.09	1.75	0.93	1.89
$^7\Sigma^-$	3.90	0.53	6.02	1.96	2.06	2.00	1.01	0.36	0.08	1.80	0.87	1.86
$^9\Pi$	3.90	0.54	6.04	1.02	3.02	2.00	0.90	0.41	0.11	1.74	0.92	3.09
$^9\Sigma^-$	3.90	0.54	6.00	1.97	2.03	2.00	0.94	0.41	0.11	1.76	0.91	1.86
$^1\Pi$	3.15	0.35	6.39	1.25	3.12	2.02	0.95	0.19	0.12	1.78	0.82	1.74

the non-bonding orbitals, 9σ and 1δ, have to be of similar energy. The major configurations of the higher-lying states of Σ^- symmetry are $(7\sigma)^2(8\sigma)^2(9\sigma)^1(10\sigma)^1(3\pi)^4(1\delta)^2$ for $^5\Sigma^-$, $(7\sigma)^2(8\sigma)^2(9\sigma)^1(10\sigma)^1(3\pi)^3(4\pi)^1(1\delta)^2$ for $^7\Sigma^-$, and $(7\sigma)^2(8\sigma)^2(9\sigma)^1(10\sigma)^1(3\pi)^2(4\pi)^2(1\delta)^2$ for the $^9\Sigma^-$ state.

The states $^5\Pi$, $^3\Pi$, and $^1\Pi$ all have the major configuration $(7\sigma)^2(8\sigma)^2(9\sigma)^1(3\pi)^4(4\pi)^1(2\delta)^2$, and thus these states represent various spin couplings. At 3.15 a.u. the major configuration contributes 70% to the wave function of the $^5\Pi$ state, only 53% for the $^3\Pi$ state, and 62% for the $^1\Pi$ state. The major configuration for the $^7\Pi$ state is $(7\sigma)^2(8\sigma)^2(9\sigma)^1(3\pi)^3(4\pi)^2(2\delta)^2$ with a contribution of only 52% at 3.15 a.u. The wave functions for the $^9\Pi$ state is $(7\sigma)^2(8\sigma)^1(9\sigma)^1(10\sigma)^1(3\pi)^3(4\pi)^2(2\delta)^2$ contributing with approximately 100%.

Altogether the low-lying states of the FeC molecule basically represent antiferromagnetic couplings between the angular momenta of the atomic fragments. Thus, most of the low-lying states of FeC are those expected when the angular momenta of the $^6D_g\mathrm{Fe}^+$ ion are coupled with those of the $^4S_u\mathrm{C}^-$ anion. However, the low-lying singlet state $^1\Delta$ with the transition energy of only 3843 cm^{-1}, and the $^1\Pi$ state with the transition energy 13384 cm^{-1} are not expected in relation to this coupling scheme. From Moore's Tables [17] it is noted that the Fe$^+$ ion has two relatively low-lying excited terms, $^4F_g(3d)^7$ at 2000 cm^{-1}, and $^4D_g(3d)^6(4s)^1$ at 7904 cm^{-1}. Coupling of the angular momenta of either of these quartet terms with the angular momenta of the $^4S_u\mathrm{C}^-$ anion can account for both the singlet states, $^1\Delta$ and $^1\Pi$.

Figure 2 presents the populations of the individual atomic orbitals of Fe and C as functions of the internuclear distance for the $^3\Delta$ ground state. As the internuclear distance is decreased below 7 a.u., it appears that population is transferred from the Fe $4s$ orbital into the C $2p\sigma$ orbital. This gives rise to a gross atomic charge that reaches a maximum of $0.54e$ at 4.2 a.u. At internuclear distances less than 4 a.u. the populations increase in the orbitals, Fe $3d\sigma$ and Fe $3d\pi$, while the populations in the orbitals C $2p\sigma$ and C $2p\pi$ correspondingly decrease. Altogether this results in a positive gross atomic charge of $0.31e$ on Fe at the equilibrium internuclear distance.

Table 4 displays the results of the population analysis for all the low-lying states at internuclear distances close to the equilibrium internuclear distance of each state. For many of the low-lying states the sum of the populations in the orbitals Fe $3d\sigma$ and C $2p\sigma$ is close to two, and correspondingly, the sum of the populations in the Fe $3d\pi$ and C $2p\pi$ is close to four or five. These orbitals are expected to form bonding σ and π orbitals that should be almost fully occupied at the equilibrium internuclear distance of the molecule. Comparison with the results in Table 3 shows that this is not the case. All the low-lying states of FeC have considerable population in the antibonding orbitals, 10σ and 4π. However, in many of the low-lying states the total occupation in the orbitals 8σ plus 10σ amounts to approximately two, and likewise, the sum of the populations in the orbitals 3π plus 4π is close to either four or five. Thus, there is sizable transfer of population from the bonding orbitals, 8σ and 3π, to the antibonding orbitals, 10σ and 4π. This indicates that the electrons tend to localize around the nuclei in agreement with the findings that the electronic structure arises from the coupling of the localized atomic angular momenta. Table 4 also shows that all the low-lying states have considerable population in the Fe $4p\sigma$ orbital. This orbital is hybridized with the Fe $4s$ orbital resulting in an orbital that is polarized away from the internuclear region. Furthermore, it is noted that charge is transferred from Fe to C in all the low-lying states resulting in positive gross atomic charges

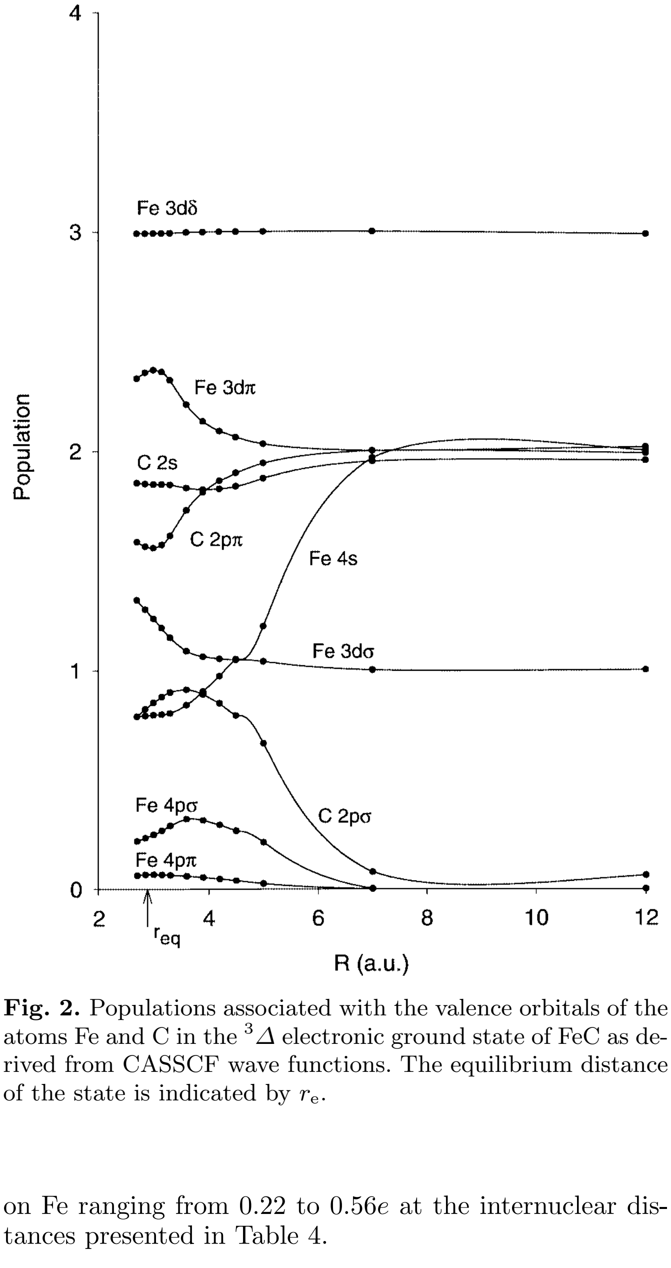

Fig. 2. Populations associated with the valence orbitals of the atoms Fe and C in the $^3\Delta$ electronic ground state of FeC as derived from CASSCF wave functions. The equilibrium distance of the state is indicated by r_e.

on Fe ranging from 0.22 to 0.56e at the internuclear distances presented in Table 4.

Balfour *et al.* [11] have used a qualitative molecular orbital diagram based on the computational results for RuC [4] to discuss the electronic structure of FeC. This diagram rationalizes the symmetry of the $^3\Delta$ ground state and the existence of the low-lying $^1\Delta$ excited state, but it cannot explain the absence of a low-lying $^1\Sigma^+$ state, or in general, the absence of low-lying states of Σ^+ symmetry. Furthermore, the rather large populations of the antibonding orbitals, 10σ and 4π, in both states $^3\Delta$ and $^1\Delta$ indicate that such a molecular orbital diagram is hardly adequate for describing the chemical bond in FeC.

The FeC molecule is polar with charge transfer from Fe to C. The electronic structure of FeC is mainly due to the antiferromagnetic coupling of the localized atomic angular momenta of the ions $^6D_g\mathrm{Fe}^+$ and $^4\mathrm{S}_u\mathrm{C}^-$. The chemical bond in the FeC molecule is described as a triple bond in the valence bond sense, *i.e.* the bonds are formed by valence bond couplings between the Fe $3d\sigma$ and Fe $3d\pi$ with the C $2p\sigma$ and C $2p\pi$

5 Results of MRCI calculations

The low-lying singlet, triplet, quintet and septet states of the FeC molecule have been further investigated by carrying out MRCI calculations using the molecular orbitals optimized in the CASSCF calculations.

From Table 3 it is noted that the 7σ orbital is approximately fully occupied in all the low-lying electronic states. Therefore we decided to keep this orbital fully occupied in all the reference configurations included in the MRCI calculations. In addition, the reference configurations for the states of Δ symmetry were required to have three electrons in the 1δ orbitals. For all other states, *i.e.* those of Σ^- and Π symmetry the 1δ orbitals were required to have two electrons in all the reference configurations.

According to Table 3, the 9σ orbital is approximately doubly occupied in the states $^5\Sigma^-$ and $^7\Sigma^-$. Therefore, the 9σ orbital is kept fully occupied in all reference configurations for these states. For the singlet and triplet states and also for the $^5\Pi$ state the antibonding 10σ orbital has been kept empty in all reference configurations. For the $^5\Delta$ state the 9σ orbital was kept singly occupied in all reference configurations. Finally, the 10σ orbital has been included in the active space for generating the reference configurations for the states $^5\Delta$ and $^5\Sigma^-$ as well as for the septet states,$^7\Sigma^-$, $^7\Pi$, and $^7\Delta$.

The number of reference configurations amounted to 74, 54, 68, and 17 for the states, $^3\Delta$, $^1\Delta$, $^5\Delta$, and $^7\Delta$. For the states $^3\Sigma^-$, $^5\Sigma^-$, and $^7\Sigma^-$ the number of reference configurations were 78, 68, and 13, respectively. Finally, the number of reference configurations for the Π states were 52 for $^1\Pi$, 84 for $^3\Pi$, 36 for $^5\Pi$, and 38 for $^7\Pi$.

In the MRCI calculations all single and double excitations were allowed from the reference configurations. This resulted in 1110904 configurations for the $^3\Delta$ state, 759230 for $^1\Delta$, 1269637 for $^5\Delta$, and 433208 for $^7\Delta$. The number of configurations included in the MRCI calculations for the $^3\Sigma^-$ state were 1308504, 1269637 for $^5\Sigma^-$, and 282114 for the $^7\Sigma^-$ state. For the Π states the number of configurations in the MRCI calculations were 661358 for $^1\Pi$, 1276387 for $^3\Pi$, 819608 for $^5\Pi$, and 913857 for $^7\Pi$.

For most of the states investigated, the MRCI calculations have been performed at the internuclear distances 2.85, 3.0, 3.15, 3.3, 3.6, 3.9, 4.2, 4.5, and 5.0 a.u. For the states $^3\Delta$ and $^1\Delta$ calculations have also been performed at 2.7 a.u. For the $^1\Delta$ state the MRCI calculations have not been performed at 4.5 and 5.0 a.u. For the states $^5\Delta$, $^7\Delta$, $^5\Sigma^-$ and $^7\Sigma^-$ MRCI calculations have not been performed at 2.85 a.u.

The potential energy curves obtained in the MRCI calculations are shown in Figure 3. The spectroscopic constants obtained by solving the Schrödinger equation for the nuclear motion numerically are presented in Table 5. Also included are the dipole moments and the gross atomic charge on Fe. The values for both the dipole moments and

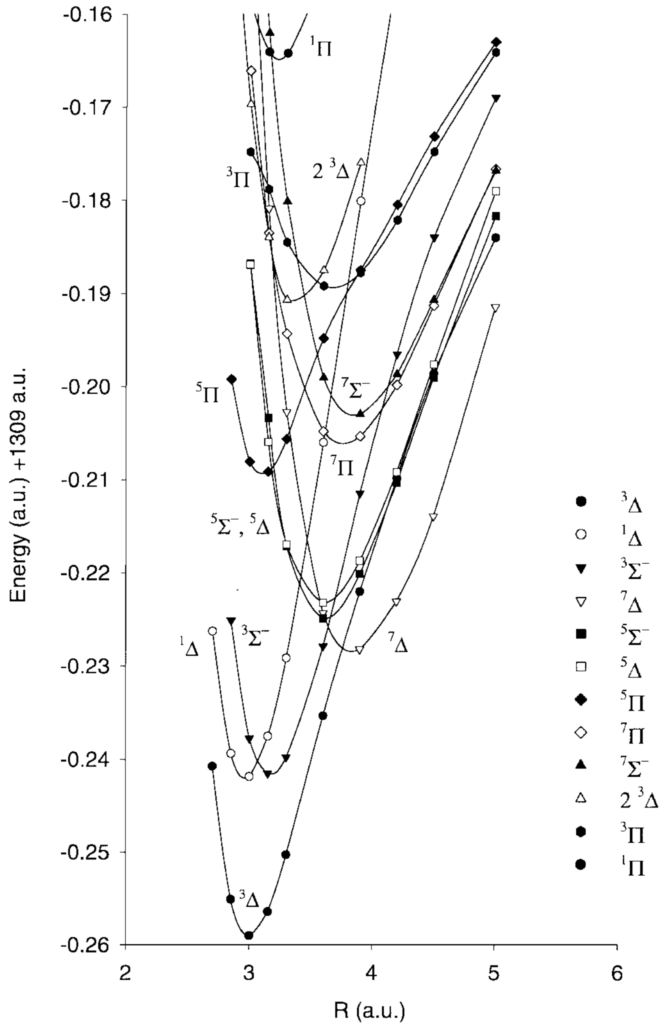

Fig. 3. Potential energy curves of 12 low-lying electronic states of the FeC molecule as derived from MRCI calculations including the relativistic corrections for the one-electron Darwin contact term and for the mass-velocity term.

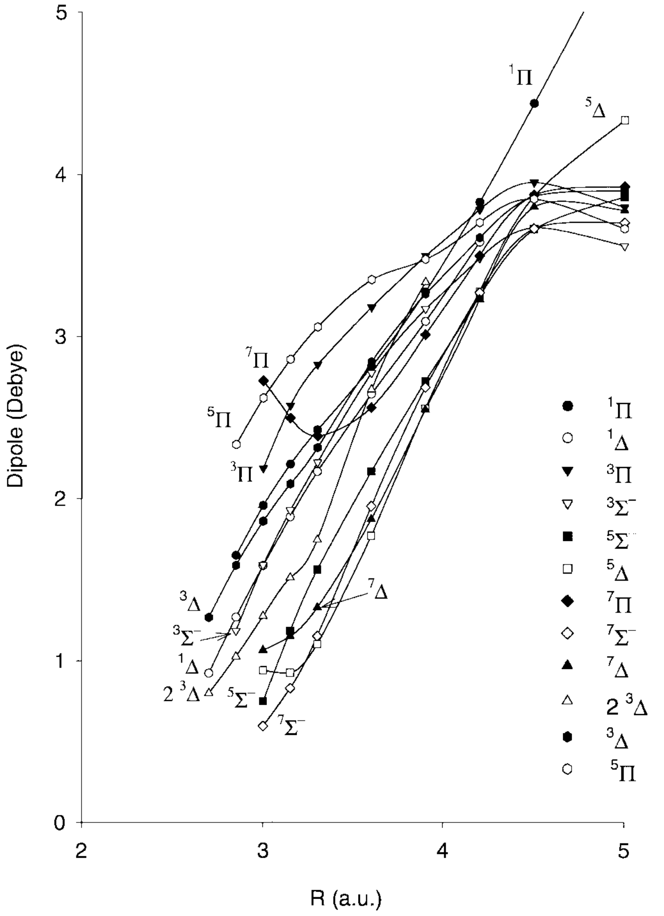

Fig. 4. Dipole moments of the $^3\Delta$ ground state and of eleven excited electronic states, $^1\Delta$, $^3\Sigma^-$, $^7\Delta$, $^5\Delta$, $^5\Sigma^-$, $^5\Pi$, $^7\Pi$, $^7\Sigma^-$, $2\,^3\Delta$, $^3\Pi$, and $^1\Pi$ of the FeC molecule as derived from MRCI wave functions.

the gross atomic charges have been derived at the equilibrium distance by interpolations. Figure 4 shows the dipole moments as functions of the internuclear distance for all the low-lying states that have been investigated in the MRCI calculations.

By comparing the results in Tables 1 and 5, and Figures 1 and 3, it is recognized that the energy splittings of the low-lying electronic states are increased and the states are interchanged in the MRCI calculations as compared to the results of the CASSCF calculations. It is especially noted that the $^3\Pi$ state is pushed up in energy, or the correlation energy gained for this state is considerably less than that gained for the $^3\Delta$ ground state. The equilibrium distances are decreased, and except for the states $^3\Pi$ and $^7\Pi$, the vibrational frequencies are increased. For the $^3\Delta$ ground state and the low-lying $^1\Delta$ state the r_e values decrease by 0.073 and 0.044 Å, and the ω_e values increase by 313 and 201 cm^{-1}, respectively. The shape of the potential energy curve for the $^5\Pi$ state is changed significantly in the MRCI calculations as compared to the CASSCF results, and this causes the decrease of r_e by 0.385 Å, and the increase of ω_e by 449 cm^{-1}. Furthermore, the energy of the $^1\Delta$ state drops below that of the $^3\Sigma^-$ state. Including the relativistic corrections, the $^3\Delta$ ground state is separated from the higher-lying states, $^1\Delta$, $^3\Sigma^-$, $^7\Delta$, $^5\Delta$, $^5\Sigma^-$, $^5\Pi$, $^7\Pi$, $^7\Sigma^-$, $2^3\Delta$, $^3\Pi$, and $^1\Pi$ by the transition energies 3718, 3840, 6728, 7857, 7484, 10865, 11623, 12286, 14809, 15305, and 20765 cm^{-1}, respectively.

Table 6 shows the contributions of the major configurations to the MRCI wave functions as functions of the internuclear distance. Table 7 shows the occupations of the natural orbitals, and Table 8 presents the results of population analysis for the low-lying electronic states as derived from the MRCI wave functions. For most of the low-lying states the weights of the major configurations are slightly decreased at short internuclear distances, and increased at larger internuclear distances as compared to the results of the CASSCF calculations. Thus, for the states $^3\Delta$ and $^1\Delta$ the weight of the major configurations $(7\sigma)^2(8\sigma)^2(9\sigma)^1(3\pi)^4(1\delta)^3$ is reduced by 3 to 5% at internuclear distances less than 3.15 a.u. and increased by 1 to 13% at larger internuclear distances.

Table 5. Spectroscopic constants of the low-lying electronic states of the FeC molecule as derived from the results of MRCI calculations. Also included are the dipole moments and the gross atomic charges on Fe.

State	Without relativistic corrections			With relativistic corrections						Dipole moment[b] (D)	Gross atomic charge on Fe[b]
	Equilibrium distance r_e(Å)	Vibrational frequency ω_e(cm^{-1})	Transition energy T_e(cm^{-1})	Equilibrium distance r_e(Å)	Vibrational frequency ω_e(cm^{-1})	Anharmonicity $\omega_e x_e$(cm^{-1})	Transition energy T_e(cm^{-1})	Dissociation energy[a] (eV)			
								D_e	D_0		
$^3\Delta$	1.589	848	0	1.585	859	−4.5	0	2.79	2.74	1.855	0.23
$^1\Delta$	1.572	933	3455	1.567	962	−16.2	3718			1.509	0.17
$^3\Sigma^-$	1.688	722	5320	1.672	761	0.3	3840			1.948	0.24
$^7\Delta$	2.036	557	6706	2.033	554	−7.1	6728			2.417	0.46
$^5\Sigma^-$	1.911	555	8219	1.891	587	−5.7	7484			2.116	0.37
$^5\Delta$	1.900	559	7855	1.897	562	−5.2	7857			1.732	0.42
$^5\Pi$	1.643	823	11205	1.637	848	−27.4	10865			2.773	0.32
$^7\Pi$	1.997	481	11759	1.991	479	−3.7	11623			2.799	0.45
$^7\Sigma^-$	2.053	502	12690	2.042	508	−3.1	12286			2.858	0.43
$2\ ^3\Delta$	1.860	833	13990	1.791	776	−13.9	14809			1.952	0.30
$^3\Pi$	1.933	373	15504	1.937	384	5.0	15305			3.245	0.44
$^1\Pi$	1.718	704	20404	1.709	706	−0.3	20705			2.302	0.27

[a] Derived as the difference between the total molecular energy at the equilibrium distance and the sum of the energies of the atoms. Basis set superposition errors are estimated to reduce the values by 0.04 eV.

[b] Values are derived at the relativistic equilibrium internuclear distances by interpolation.

Table 8 shows that in all the low-lying states there is charge transfer from Fe to C resulting in gross atomic charges on Fe in the range 0.17 to 0.47e. Comparison of Tables 4 and 8 reveals that the positive gross atomic charge on Fe is reduced in the MRCI relative to the CASSCF calculations by 0.04 to 0.11e. Furthermore, from Tables 3 and 7 it is noted that the populations of the bonding orbitals 8σ and 3π are increased, and those of the antibonding orbitals 10σ and 4π are decreased. However, these changes do not lead to a different interpretation of the interaction between the atoms Fe and C, since the antibonding orbitals retain substantial populations. This is also verified by comparing the results of the population analysis presented in Tables 4 and 8.

Figure 4 shows that for all the low-lying electronic states investigated in the MRCI calculations the values of the dipole moments are strongly dependent on the internuclear distance.

6 Comparison with experiments

Based on the results of the MRCI calculation, the equilibrium distance for the $^3\Delta$ ground state is derived as 3.002 a.u. or 1.589 Å without relativistic corrections, and 2.996 a.u. or 1.585 Å when the relativistic corrections are included. This compares well with the reported mean internuclear distances derived by Balfour *et al.* [11]: 1.596 Å for $^3\Delta_3$ and 1.591 Å for $^3\Delta_2$. The vibrational frequency for the $^3\Delta$ ground state is derived as 848 cm^{-1} from the MRCI calculations without relativistic corrections, increasing to 859 cm^{-1} when the relativistic effects are taken into account. Balfour *et al.* [11] have estimated the ground state vibrational frequency of FeC to be 805 cm^{-1}.

The equilibrium distance for the $^1\Delta$ excited state is derived as 2.970 a.u. or 1.572 Å without relativistic correction and as 2.961 a.u. or 1.567 Å including the relativistic corrections. Balfour *et al.* [11] determined the equilibrium distance for the $^1\Delta$ excited state to be 1.595 Å. The vibrational frequency of the $^1\Delta$ state is derived as 933 cm^{-1} increasing to 962 cm^{-1} when the relativistic corrections are taken into account.

The excited 2 $^3\Delta$ state identified in the present work is determined as the second root of the matrix used to determine the ground state, and therefore the energy of the 2 $^3\Delta$ is less accurate than that of the ground state. The transition energy between the $^3\Delta$ ground state and the excited 2 $^3\Delta$ state is derived as 14809 cm^{-1}, the vibrational frequency as 776 cm^{-1}, and the equilibrium distance as 1.791 Å. These values indicate that the $^3\Delta_3$ state identified by Brugh and Morse [13] with $T_e = 13168$ cm^{-1}, $\omega_e = 732$ cm^{-1}, and $r_e = 1.753$ Å probably is the 2 $^3\Delta$ state.

The dissociation energy has been determined on the basis of the results of the MRCI calculations by subtracting the sum of the energies of the atoms in their ground terms from the energy of the molecule at the equilibrium distance. The energies of the atoms have been derived in MRCI calculations equivalent to those performed for the molecule. The dissociation energy, D_e, of FeC in its $^3\Delta$

Table 6. The contributions of the major configurations to the MRCI wave functions describing the $^3\Delta$ ground state and the low-lying excited states of the FeC molecule as functions of the internuclear distance.

State	Valence shell configuration							Contribution of valence shell configuration (%)						
	7σ	8σ	9σ	10σ	3π	4π	1δ	Inter nuclear distance (a.u.)						
	(C s)	(σ)	(Fe σ)	(σ^*)	(π)	(π^*)		2.7	2.85	3.0	3.15	3.3	3.6	3.9
$^3\Delta$	2	2	1	0	4	0	3	76	72	67	61	54	39	29
$^3\Sigma^-$	2	2	2	0	4	0	2		68	62	57	51	39	28
$^1\Delta$	2	2	1	0	4	0	3	76	72	67	61	54	41	30
$^5\Delta$	2	2	1	0	3	1	3			59	49	42	35	31
	2	1	1	1	4	0	3			11	12	12	9	7
$^3\Pi$	2	2	1	0	4	1	2			68	64	60	51	45
$^7\Delta$	2	1	1	1	3	1	3			34	36	36	33	28
	2	2	1	0	2	2	3			42	38	35	34	37
$^5\Pi$	2	2	1	0	4	1	2		76	73	69	65	51	39
$^5\Sigma^-$	2	2	1	1	4	0	2			50	26	11	6	4
	2	2	2	0	3	1	2			11	33	46	45	41
$^7\Pi$	2	2	1	0	3	2	2			73	59	50	46	
$^7\Sigma^-$	2	2	1	1	3	1	2			68	60	49	38	21
	2	2	2	0	2	2	2			6	12	21	31	50
$^1\Pi$	2	2	1	0	4	1	2		73	68	63	58	49	41

Table 7. Occupations in the natural orbitals for the low-lying electronic states of FeC as derived in MRCI calculations. Also shown are the dipole moments at the respective internuclear distances.

State	Internuclear distance (a.u.)	Dipole moment (D)	Population in								
			7σ (C s)	8σ (σ)	9σ (Fe σ)	10σ (σ^*)	11σ	3π (π)	4π (π^*)	5π	1δ
$^3\Delta$	3.00	1.862	1.97	1.88	1.00	0.11	0.01	3.53	0.46	0.01	2.98
$^3\Sigma^-$	3.15	1.928	1.96	1.88	1.93	0.12	0.02	3.41	0.59	0.03	2.00
$^1\Delta$	3.00	1.589	1.96	1.87	1.00	0.11	0.02	3.52	0.47	0.01	2.98
$^5\Delta$	3.60	1.772	1.96	1.43	1.00	0.55	0.01	2.58	1.40	0.02	2.98
$^3\Pi$	3.60	3.180	1.97	1.78	1.00	0.20	0.01	3.48	1.49	0.02	2.00
$^7\Delta$	3.90	2.547	1.96	1.32	0.99	0.66	0.02	2.17	1.79	0.02	2.98
$^5\Pi$	3.15	2.859	1.96	1.84	1.01	0.13	0.01	3.66	1.30	0.03	2.00
$^5\Sigma^-$	3.60	2.166	1.96	1.60	1.95	0.39	0.02	2.57	1.40	0.03	2.00
$^7\Pi$	3.90	3.010	1.96	1.45	1.00	0.53	0.02	3.05	1.90	0.03	2.00
$^7\Sigma^-$	3.90	2.686	1.97	1.45	1.97	0.54	0.02	2.13	1.84	0.03	2.00
$^1\Pi$	3.15	2.211	1.96	1.84	1.00	0.15	0.01	3.62	1.34	0.03	2.00
2 $^3\Delta$	3.15	1.514	1.96	1.60	1.22	0.15	0.01	2.91	1.07	0.02	2.98

ground state is determined as 2.88 eV not considering relativistic effects, and as 2.79 eV when the relativistic effects are taken into account. The corresponding values for D_0 are 2.83 and 2.74 eV, respectively. Basis set superposition errors will reduce these values further by approximately 0.04 eV. The values are somewhat lower than the upper limit to the bond energy, 3.9 ± 0.3 eV reported by Brugh and Morse [13].

The dipole moment for the $^3\Delta$ ground state at the equilibrium distance has been derived from the results of the MRCI calculations by interpolation as $1.855D$. The corresponding results for all the low-lying states are reported in Table 5.

7 Conclusions

The electronic structure and the nature of the chemical bond in the FeC molecule have been elucidated by performing all electron *ab initio* MCSCF (CASSCF) and MRCI calculations. Thus, 15 electronic states of FeC were investigated by performing CASSCF calculations, while 12 of these states were further investigated by performing MRCI calculations.

The electronic structure of FeC is consistent with antiferromagnetic coupling of the localized angular momenta of the ions $^6D_g\mathrm{Fe}^+$ and $^4S_u\mathrm{C}^-$. The chemical bond in the FeC molecule can be described as a triple bond in the valence bond sense, *i.e.* the bonds are formed by valence

Table 8. Results of population analysis for the low-lying electronic states of FeC as derived from MRCI calculations. Also included are the dipole moments, the gross atomic charge on Fe, and the number of d electrons on Fe at the respective internuclear distances.

State	Internuclear distance (a.u.)	Gross atomic charge on Fe	Number of d electrons on Fe	Population								
				Fe						C		
				$3d\sigma$	$3d\pi$	$3d\delta$	$4s$	$4p\sigma$	$4p\pi$	$2s$	$2p\sigma$	$2p\pi$
$^3\Delta$	3.00	0.23	6.66	1.28	2.38	2.99	0.79	0.24	0.08	1.80	0.85	1.54
$^3\Sigma^-$	3.15	0.24	6.17	1.58	2.59	2.00	1.28	0.20	0.11	1.81	1.05	1.34
$^1\Delta$	3.00	0.17	6.66	1.34	2.33	2.99	0.89	0.19	0.08	1.78	0.77	1.59
$^5\Delta$	3.60	0.42	6.24	1.07	2.17	3.00	0.87	0.37	0.10	1.76	0.90	1.73
$^3\Pi$	3.60	0.44	6.28	1.10	3.17	2.00	0.91	0.26	0.10	1.80	0.89	1.73
$^7\Delta$	3.90	0.47	6.14	1.08	2.07	2.99	0.92	0.35	0.12	1.76	0.89	1.79
$^5\Pi$	3.15	0.33	6.37	1.35	3.01	2.00	0.79	0.26	0.26	1.78	0.79	1.72
$^5\Sigma^-$	3.60	0.37	6.04	1.83	2.21	2.00	1.15	0.30	0.13	1.78	0.89	1.68
$^7\Pi$	3.90	0.45	6.09	1.07	3.02	2.00	0.98	0.32	0.15	1.76	0.84	1.83
$^7\Sigma^-$	3.90	0.43	5.99	1.93	2.06	2.00	1.11	0.33	0.14	1.77	0.82	1.82
$^1\Pi$	3.15	0.27	6.44	1.34	3.10	2.00	0.93	0.18	0.17	1.73	0.79	1.72
$2\,^3\Delta$	3.15	0.28	6.46	1.24	2.23	2.99	0.94	0.22	0.09	1.78	0.78	1.69

bond couplings between the Fe $3d\sigma$ and Fe $3d\pi$ with the C $2p\sigma$ and C $2p\pi$.

The electronic ground state of the FeC molecule has been verified as being $^3\Delta$ with the leading configuration $(7\sigma)^2(8\sigma)^2(9\sigma)^1(3\pi)^4(1\delta)^3$. The spectroscopic constants of the FeC molecule in the $^3\Delta$ ground state have been determined as $r_e = 1.585$ Å and $\omega_e = 859$ cm^{-1}. The $^3\Delta$ ground state is separated from the excited states, $^1\Delta$, $^3\Sigma^-$, $^7\Delta$, $^5\Delta$, $^5\Sigma^-$, $^5\Pi$, $^7\Pi$, $^7\Sigma^-$, $2\,^3\Delta$, $^3\Pi$, and $^1\Pi$ by the transition energies 3718, 3840, 6728, 7857, 7484, 10865, 11623, 12286, 14809, 15305, and 20765 cm^{-1}, respectively.

The dissociation energy, D_e is derived as 2.79 eV, and D_0 as 2.74 eV. The basis set superposition errors are estimated to reduce these values by 0.04 eV.

The spectroscopic constants of the $^3\Delta$ ground state and the low-lying $^1\Delta$ excited state are in good agreement with the values measured by Balfour *et al.* [11].

The computations have been performed at the Computing Services Center at Texas A&M University, and at UNI-C at the Technical University of Denmark supported by the Danish Natural Research Council. I.S. acknowledges the Danish Natural Research Council and the Computing Services Center at Texas A&M University for funding the computational work. 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. CRG 940581 for international collaboration in research.

References

1. I. Shim, K.A. Gingerich, J. Chem. Phys. **76**, 3833 (1982).
2. I. Shim, K.A. Gingerich, J. Chem. Phys. **81**, 5937 (1984).
3. I. Shim, K.A. Gingerich, Surf. Sci. **156**, 623 (1985).
4. I. Shim, H.C. Finkbeiner, K.A. Gingerich, J. Phys. Chem. **91**, 3171 (1987).
5. I. Shim, in: *Understanding Molecular Properties*, edited by J. Avery, J.P. Dahl, A.E. Hansen (Reidel, Holland, 1987), pp. 555-583.
6. I. Shim, K.A. Gingerich, Z. Phys. D **12**, 373 (1989).
7. I. Shim, K.A. Gingerich, Int. J. Quantum Chem. **23S**, 409 (1989).
8. I. Shim, K.A. Gingerich, Int. J. Quantum Chem. **42**, 349 (1992).
9. I. Shim, M. Pelino, K.A. Gingerich, J. Chem. Phys. **97**, 9240 (1992).
10. I. Shim, K.A. Gingerich, J. Chem. Phys. **106**, 8093 (1997).
11. W.J. Balfour, J. Cao, C.V.V. Prasad, C.X.W. Qian, J. Chem. Phys. **103**, 4046 (1995).
12. M.D. Allen, T.C. Pesch, L.M. Ziurys, Astrophys. J. **472**, L57 (1996)
13. D.J. Brugh, M.D. Morse, J. Chem. Phys. **107**, 9772 (1998).
14. K. Andersson, M.R.A. Blomberg, M.P Fülscher, V. Kellö, R. Lindh, P.-Å. Malmquist, J. Noga, J. Olsen, B.O. Roos, A.J. Sadley, P.E.M. Siegbahn, M. Urban, P.O. Widmark, MOLCAS, version 3 (University of Lund, Sweden, 1994).
15. A.J.H. Wachters, J. Chem. Phys. **52**, 1033 (1970).
16. S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965).
17. C.E Moore, Natl. Bur. Stand. Circ. No 467, **2** (1952).