

Theoretical investigation of the ground and low-lying excited states of nickel carbide, NiC

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The electronic structure and bonding of 19 states of the diatomic nickel carbide (NiC) has been studied by multireference methods. Potential energy curves have been constructed for all states, whereas for the three lowest states of symmetries $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ well separated from the rest of the states, special attention was paid through the use of very large basis sets and the calculation of core-valence correlation and scalar relativistic effects. The recommended binding energies for these states are 91, 67, and 54 kcal/mol with respect to the ground state atoms. Our results in general can be considered in fair agreement with the limited experimental findings. © 2007 American Institute of Physics. [DOI: 10.1063/1.2723114]

I. INTRODUCTION

According to Cotton and Wilkinson,¹ “the transition elements may be defined strictly as those that, as elements, have partly filled d or f shells.” Therefore, the first row $3d$ -transition metals consist of eight elements, Sc ($Z=21$; $4s^23d^1$) to Ni ($Z=28$; $4s^23d^8$). Relaxing the above definition to include Cu in the $3d$ series because Cu^{2+} has a $3d^9$ configuration,¹ NiC is the penultimate diatomic carbide in the MC sequence, $M=\text{Sc}$ to Cu . Having completed the theoretical *ab initio* study of ScC ,^{2(a)} TiC ,^{2(b)} VC ,^{2(c)} CrC ,^{2(d)} MnC ,^{2(e)} $\text{FeC}^{2(f,2(g)}$ and CoC ,^{2(h)} while the investigation of CuC [Ref. 2(i)] is in progress, we herein present high level first principles calculations on the ground and 18 excited states of NiC.}}}}}}

As far as we know there are two experimental and seven theoretical studies on NiC. In 2001 Brewster and Ziurys recorded for the first time the rotational spectrum of the ground state ($X^1\Sigma^+$) of NiC,³ reporting a bond distance $r_0 = 1.6308 \text{ \AA}$. A year later Brugh and Morse provided the first analysis of the optical spectrum of NiC.⁴ They determined spectroscopic parameters (r_e , ω_e , $\omega_e x_e$, and a_e), the ionization energy of the $X^1\Sigma^+$ state, and a lower bound for the dissociation energy, $D_0 \geq 77.0 \text{ kcal/mol}$. They also found that the excited electronic states of NiC display a complicated pattern of vibronic levels due to extensive perturbations among the $\Omega=0^+$ excited states, making the identification of these states unfeasible.

The first theoretical investigation on NiC was reported in 1982 by Kitaura *et al.* using the generalized valence bond approach.⁵ They predicted, correctly, that the ground state symmetry of NiC is $^1\Sigma^+$, but the reported dissociation energy $D_e=23 \text{ kcal/mol}$ and equilibrium bond distance $r_e=1.8 \text{ \AA}$ deviate significantly from the “true” values. A few years later Panas *et al.*⁶ using limited complete active space self-consistent field (CASSCF)+configuration interaction (CI) methods in conjunction with an effective core potential for

the Ni atom, they obtained $r_e=1.699 \text{ \AA}$ and $D_e=75.0 \text{ kcal/mol}$ for a $^1\Sigma^+$ state of NiC. Note, however, that the D_e value of these workers is given with respect to Ni $a^3D(3d^94s^1)$ and not with respect to the ground state of Ni $a^3F(3d^84s^2)$, and this is important (*vide infra*).

Shim and Gingerich in 1989 performed CISD/[$8s6p3d/\text{Ni};4s3p1d/\text{C}$] all electron calculations on the isovalent series NiC, NiSi, and NiGe.⁷ For the NiC they calculated 12 states reconfirming that the ground state is of $^1\Sigma^+$ symmetry,⁵ but their results are only qualitative due to the nature of the methodology employed and small basis sets.

About a decade later Sosa *et al.*⁸ reported density functional theory calculations (DFT/BP86) on the $M_n\text{C}$ carbides, $M=\text{Fe}$, Ni , Cu , and Ti and $n=1, 5$, or 7 . For the NiC they considered two states (symmetries are not given), but the results are rather disappointing if one considers that they obtained a binding energy for the lower state of 141.4 kcal/mol , about 50 kcal/mol higher than the true value (*vide infra*).

Relatively recently Shim and Gingerich reexamined the NiC problem by performing CASSCF/[$8s6p3d1f/\text{Ni};4s3p1d/\text{C}$] calculations reporting geometries, spectroscopic parameters, and dipole moments on 16 low-lying states.⁹ For the $X^1\Sigma^+$ state only they extended their computations to the CASSCF+1+2(=MRCI) level of theory including Darwin and mass-velocity relativistic corrections. In general, their results are mostly qualitative suffering from lack of (dynamical) correlation and inadequate basis sets. For the ground state they predict $D_e=2.76 \text{ eV}$ ($=63.6 \text{ kcal/mol}$) and $r_e=1.621 \text{ \AA}$.

In 2001 Borin examined the $X^1\Sigma^+$ and $A^1\Pi$ states of NiC through MRCI calculations coupled with a [$8s6p4d1f/\text{Ni}$ cc-pTZ/C] basis set;¹⁰ scalar relativistic effects were taken into account through the Cowan-Griffin approach. Borin reports potential energy curves, spectroscopic constants, transition dipole moments, and radiative lifetimes for several vibrational levels of the $A^1\Pi$ state. In the same spirit and using exactly the same methodology a few years

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later, Borin and de Macedo¹¹ investigated six more states $a^3\Pi$, $B^1\Phi$, $b^3\Phi$, $c^3\Sigma^+$, $C^1\Delta$, and $d^3\Delta$. Pertinent results from Refs. 10 and 11 will be contrasted with our own as we go along.

From the above short exposition of the experimental and theoretical results on NiC, it is clear that there is enough room for a more systematic and quantitative theoretical investigation of the electronic structure and bonding of this interesting system. Specifically, we present high level multi-reference variational calculations on a total of 19 states of NiC, covering an energy range of 3.3 eV. All calculated states correlate adiabatically to the ground state atoms Ni(a^3F)+C(3P) which give rise to a manifold of $36^{2S+1}|A|$ states.

Following the philosophy of our previous work on the 3d-diatomic metalcarbides,² for all states examined we report complete potential energy curves (PEC), binding energies, spectroscopic parameters, and dipole moments; the description of bonding is also one of the goals of the present work.

In Sec. II we define the technical approach followed, in Sec. III we discuss our results, and in Sec. IV we recapitulate our findings.

II. BASIS SETS AND METHODS

For the Ni atom the averaged natural orbital (ANO) basis set (20s15p10d6f4g) of Bauschlicher, Jr.¹² and the correlation consistent basis set cc-pV5Z=(28s20p12d4f3g2h1i) of Balabanov and Peterson¹³ were used. These were combined with the correlation consistent basis sets of Dunning, Jr. for the C atom, namely, cc-pVQZ=(12s6p3d2f1g) and cc-pV5Z=(14s8p4d3f2g1h),¹⁴ generally contracted to $[7s6p4d3f2g/Ni\ 5s4p3d2f1g/C]=4Z$ and $[9s8p6d4f3g2h1i/Ni\ 6s5p4d3f2g1h/C]=5Z$, comprising 139 and 244 spherical Gaussian one electron functions, respectively.

Apart from a full-CI approach, obviously unrealistic for NiC, the only *ab initio* method capable of coping with an inherently multireference system such as NiC and for any internuclear distance, is a multiconfiguration self-consistent field (MCSCF) one followed by CISD out of the MCSCF space. The CASSCF variant of MCSCF is employed here as a reference wave function, while “hard” (dynamical) correlation was extracted by single and double excitations out of the CASSCF wave functions (MRCI). The CASSCF wave function was constructed by allotting the 14 “valence” electrons to ten valence orbitals (one 4s+five 3d on Ni, and one 2s+three 2p on C). The zeroth order (CAS) space(s) range from 572($^5\Pi$) to 1740($^3\Pi$) configuration functions (CF), with MRCI valence spaces ranging from $58\times 10^6(^1\Delta)$ to $387\times 10^6(^3\Pi)$ CFs. By applying the internal contraction approximation (icMRCI),¹⁵ the size of the CI spaces is reduced by more than an order of magnitude, thus making the computations tractable. To account for the semicore ($3s^23p^6$) correlation effects, icMRCI calculations were performed by including the $3s^23p^6$ Ni electrons in the CI procedure. For these calculations the usual ANO basis set of Bauschlicher, Jr. (without specially tuned core functions) was used,¹² as

well as the weighted-core cc-pwCV5Z basis set for Ni by Balabanov and Peterson¹³ combined with the cc-pV5Z for C,¹⁴ contracted to $[11s10p8d5f4g3h2i/Ni\ 6s5p4d3f2g1h/C]=C5Z$. We will refer to these calculations as C-MRCI/4Z or C-MRCI/C5Z depending on the basis set used. The extensive Balabanov-Peterson basis set was only employed for the three lower states $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ around equilibrium.

The effects of relativity for the three lower states, i.e., $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$, were examined through the second order Douglas-Kroll-Hess (DKH2) approximation^{16,17} for both MRCI and C-MRCI quality wave functions. For this kind of calculations the appropriately contracted Balabanov-Peterson¹³ basis sets cc-pV5Z-DK and cc-pwCV5Z-DK were used for Ni coupled with the cc-pV5Z-DK for C, namely, $[9s8p6d4f3g2h1i/Ni\ 6s5p4d3f2g1h/C]$ and $[11s10p8d5f4g3h2i/Ni\ 6s5p4d3f2g1h/C]$, respectively. We will refer to these basis sets as 5Z-DK and C5Z-DK, respectively.

All calculations were done under C_{2v} symmetry constraints; however, the CASSCF wave functions possess correct angular momentum symmetry, i.e., $|A|=0(\Sigma^\pm)$, $1(\Pi)$, $2(\Delta)$, and $3(\Phi)$. This means that Π and Φ states are linear combinations of B_1 and B_2 symmetries, Δ combinations of A_1 and A_2 symmetries, whereas Σ^+ and Σ^- correspond to A_1 and A_2 species, respectively. Of course, MRCI wave functions do not display in general pure spatial angular momentum symmetry, but A_1 (or A_2) and B_1 (or B_2). The CASSCF state average¹⁸ (SA) approach was applied for certain excited states whenever strong interactions were observed within states of the same symmetry species.

For the $a^3\Pi$ state the spin-orbit (SO) splittings were calculated using the previous uncontracted basis sets of Bauschlicher, Jr.¹² and Dunning, Jr.¹⁴ (but with the *g* functions removed) at the MRCI/(20s15p10d6f/Ni 12s6p3d2f/C) level of theory through the Breit-Pauli operator. Also, the basis set superposition error (BSSE) of the $X^1\Sigma^+$ was estimated through the counterpoise technique.¹⁹

Finally, due to the relatively large number of valence electrons (14), we encountered significant size nonextensivity effects: On the average about 13 mE_h at the MRCI level which reduces to about 3 mE_h by including the Davidson correction²⁰ for unlinked clusters.

All calculations were performed by the MOLPRO 2002 suite of codes.²¹

III. RESULTS AND DISCUSSION

The ground state $a^3F(4s^23d^8)$ and the first excited state $a^3D(4s^13d^9)$ of the Ni atom are practically degenerate with $\Delta E(a^3D_{M_j=3}\leftarrow a^3F_{M_j=4})=204.786\text{ cm}^{-1}$ ($=0.0254\text{ eV}$).²² The M_j -averaged energy splitting $a^3D\leftarrow a^3F$ at the MRCI [MRCI+Davidson correction (+Q)]/[7s6p4d3f2g]_{Ni} level is $-0.0204(-0.031)\text{ eV}$ in good agreement with the experimental value of -0.0298 eV .²²

Table I lists total energies (E), equilibrium distances (r_e), dissociation energies (D_e) with respect to ground state atoms, Mulliken charges on Ni (q_{Ni}), harmonic frequencies (ω_e), and energy gaps (T_e) at the CASSCF, icMRCI, and icMRCI+Q levels of theory of 19 $^{58}\text{Ni}^{12}\text{C}$ molecular states.

TABLE I. Absolute energies E (hartree), bond lengths r_e (Å), binding energies D_e (kcal/mol), harmonic frequencies ω_e (cm^{-1}), total Mulliken charges on Ni q_{Ni} , dipole moments μ (Debye), and energy differences T_e (kcal/mol) of $19^{58}\text{Ni}^{12}\text{C}$ (states in ascending MRCI/4Z energy order). Experimental and other theoretical results are also included.

State	Method ^a	$-E$	r_e	D_e	ω_e	q_{Ni}	$\langle\mu\rangle/\mu_{\text{FF}}^b$	T_e
$X^1\Sigma^+$	CASSCF/4Z	1544.655 07	1.658	47.3	796.5	0.22	2.34/2.34	0.0
	CASSCF/5Z	1544.656 52	1.658	47.5	796.4	0.17	2.38/2.38	0.0
	MRCI/4Z	1545.100 91	1.637	86.4	885.7	0.16	1.95/2.25	0.0
	MRCI+Q/4Z	1545.145 1	1.636	92.7			/2.07	0.0
	MRCI/5Z	1545.120 75	1.634	87.6	890.8	0.08	1.98/2.31	0.0
	MRCI+Q/5Z	1545.166 1	1.633	94.1			/2.16	0.0
	RCCSD(T)/5Z	1545.183 16	1.634	99.5	851		/1.55	0.0
	MRACPF/5Z	1545.168 78	1.632	94.0	900	0.01	1.61/1.98	0.0
	MRCI+DKH2/5Z	1557.337 85	1.619	86.9	908.9	0.07	1.90/2.22	0.0
	MRCI+DKH2+Q/5Z	1557.383 7	1.618	93.2			/2.05	0.0
	C-MRCI/4Z ^c	1545.426 27	1.634	86.9	903.2		2.02/2.31	0.0
	C-MRCI+Q/4Z ^c	1545.504 3	1.631	95.4			/2.18	0.0
	C-MRCI/C5Z ^c	1545.538 40	1.636	84.9	901.8		2.09/2.40	0.0
	C-MRCI+Q/C5Z ^c	1545.623 8	1.633	93.8			/2.29	0.0
	C-MRCI+DKH2/C5Z ^c	1557.756 33	1.621	84.0	916.1		2.00/2.30	0.0
	C-MRCI+DKH2+Q/C5Z ^c	1557.842 3	1.619	92.7			/2.20	0.0
	C-MRACPF+DKH2/C5Z ^c	1557.858 29	1.617	93.6	928		1.59/1.90	
	C-MRCI ^d	1557.432 2	1.627	68.7	937		1.266	
	Expt. ^e			1.630 8				
	Expt. ^f			1.627 29	≥ 78.2	875.155		
$a^3\Pi$	CASSCF/4Z	1544.620 26	1.963	26.7	489.3	0.44	2.50/2.50	21.8
	CASSCF/5Z	1544.621 78	1.963	26.7	490.1	0.52	2.49/2.49	21.8
	MRCI/4Z	1545.068 00	1.620	66.0	954	0.19	1.84/3.28	20.7
	MRCI+Q/4Z	1545.113 9	1.615	73.1			/3.50	19.6
	MRCI/5Z	1545.087 52	1.617	67.4	957	0.17	1.80/3.31	20.9
	MRCI+Q/5Z	1545.134 4	1.613	74.7			/3.54	19.9
	MRACPF/5Z	1545.139 10	1.607	75.9	977	0.09	1.47/3.39	18.6
	MRCI+DKH2/5Z	1557.298 96	1.607	63.1	971	0.17	1.85/3.10	24.4
	MRCI+DKH2+Q/5Z	1557.346 4	1.601	70.3			/3.30	23.4
	C-MRCI/4Z ^c	1545.392 39	1.615	66.0	968		1.88/3.25	21.3
	C-MRCI+Q/4Z ^c	1545.471 4	1.609	74.9			/3.49	20.6
	C-MRCI/C5Z ^c	1545.504 23	1.617	63.8	972		1.86/3.21	21.4
	C-MRCI+Q/C5Z ^c	1545.590 4	1.610	73.0			/3.57	20.9
	C-MRCI+DKH2/C5Z ^c	1557.716 50	1.606	59.4	981		1.92/3.07	25.0
	C-MRCI+DKH2+Q/C5Z ^c	1557.803 3	1.598	68.4			/3.28	24.5
	C-MRACPF+DKH2/C5Z ^c	1557.821 90	1.590	70.8	1018		1.36/3.21	22.9
	C-MRCI ^d	1557.396 0	1.620	46.4	937			22.6
$A^1\Pi$	CASSCF/4Z	1544.623 90	1.952	29.0	515.2	0.44	2.52/2.52	19.6
	CASSCF/5Z	1544.625 42	1.952	29.0	516.2	0.52	2.51/2.51	19.5
	MRCI/4Z	1545.050 42	1.633	54.9	996	0.20	1.17/1.85	31.7
	MRCI+Q/4Z	1545.093 5	1.624	60.1			/2.03	32.4
	MRCI/5Z	1545.070 03	1.630	56.4	995	0.21	1.14/1.87	31.8
	MRCI+Q/5Z	1545.114 2	1.621	62.0			/2.06	32.6
	MRACPF/5Z	1545.116 66	1.617	61.8	1068	0.14	1.12/2.11	32.7
	MRCI+DKH2/5Z	1557.281 91	1.624	52.4	969	0.22	1.35/2.03	35.1
	MRCI+DKH2+Q/5Z	1557.326 4	1.613	57.8			/2.19	35.9
	C-MRCI/4Z ^c	1545.379 93	1.626	55.0	972		1.20/1.79	29.1
	C-MRCI+Q/4Z ^c	1545.451 2	1.615	62.0			/1.98	33.3
	C-MRCI/C5Z ^c	1545.487 00	1.626	52.8	1016		1.19/1.78	32.3
	C-MRCI+Q/C5Z ^c	1545.570 4	1.615	60.3			/1.98	33.5
	C-MRCI+DKH2/C5Z ^c	1557.699 70	1.622	48.9	940		1.41/1.96	35.5
	C-MRCI+DKH2+Q/C5Z ^c	1557.783 6	1.607	56.0			/2.06	36.8
	C-MRACPF+DKH2/C5Z ^c	1557.798 34	1.602	56.0	1087		1.26/2.20	37.8
	C-MRCI ^d	1557.389 4	1.773	42.0	539		1.822	27.0
$3^3\Pi$	CASSCF	1544.593 82	1.774	11.0	633	0.31	2.13/2.43	38.4
	MRCI	1545.039 49	1.721	48.5	1243	0.22	2.00/3.33	38.5

TABLE I. (Continued.)

State	Method ^a	$-E$	r_e	D_e	ω_e	q_{Ni}	$\langle\mu\rangle/\mu_{\text{FF}}^b$	T_e
	MRCI+Q	1545.084 9	1.719	55.1			/3.42	37.8
4 $^3\Sigma^+$	CASSCF	1544.623 47	1.963	27.5	527.2	0.43	2.20/2.20	19.8
	MRCI	1545.039 43	1.669	47.8	874	0.12	0.75/0.88	38.6
	MRCI+Q	1545.079 4	1.662	51.4			/1.05	41.3
	C-MRCI ^d	1557.382 8	1.843	37.8	561			31.0
5 $^3\Phi$	CASSCF	1544.615 22	1.972	22.8	471.1	0.42	2.62/2.62	25.0
	MRCI	1545.038 34	1.723	47.4	843.9	0.26	1.96/2.82	39.3
	MRCI+Q	1545.081 4	1.702	53.2			/2.90	40.0
	C-MRCI ^d	1557.383 5	1.748	38.3	673			30.6
6 $^1\Phi$	CASSCF	1544.617 78	1.965	24.8	500.8	0.42	2.56/3.64	23.4
	MRCI	1545.037 19	1.766	46.9	675.2	0.28	1.80/2.57	40.0
	MRCI+Q	1545.078 9	1.737	51.5			/2.54	41.6
	C-MRCI ^d	1557.385 8	1.784	39.9	603			29.0
7 $^5\Delta$	CASSCF	1544.612 88	2.029	20.9	514.2	0.48	2.84/2.84	26.5
	MRCI	1545.035 50	1.685	45.3	1078.4	0.32	2.83/4.45	41.0
	MRCI+Q	1545.078 6	1.676	50.8			/4.56	41.7
8 $^1\Pi$	CASSCF	1544.568 75	1.750	-3.8	707.5	0.27	1.98/2.42	54.2
	MRCI	1545.024 47	1.713	39.8	973.6	0.20	1.72/2.74	48.0
	MRCI+Q	1545.072 4	1.712	47.9				45.6
9 $^3\Delta$	CASSCF	1544.615 34	2.037	24.2	516.8	0.49	3.06/3.06	24.9
	MRCI _G	1545.024 28	1.696	39.1	1734	0.31	2.73/4.57	48.1
	MRCI+Q _G	1545.066 6	1.693	43.9			/4.78	49.3
	MRCI _L	1545.016 49	1.936	34.2	486.9	0.43	2.62/3.13	53.0
	MRCI+Q _L	1545.051 7	1.916	34.5			/3.13	58.6
	C-MRCI ^d	1557.366 7	1.970	27.7	529			41.1
10 $^1\Delta$	CASSCF	1544.616 32	2.042	23.1	518.0	0.50	3.15/3.15	24.3
	MRCI	1545.016 93	1.955	33.6	521.8	0.44	2.74/3.17	52.7
	MRCI+Q	1545.051 8	1.945	34.0			/3.16	58.6
	C-MRCI ^d	1557.366 7	1.992	27.9	529			41.0
11 $^3\Sigma^+$	CASSCF	1544.591 27	1.885	9.56	563.7	0.40	1.45/0.97	40.0
	MRCI	1545.015 81	1.746	34.0	978.5	0.23	0.71/1.25	53.4
	MRCI+Q	1545.057 1	1.734	38.0			/1.38	55.3
12 $^5\Pi$	CASSCF	1544.610 61	2.042	20.4	510.0	0.48	2.63/2.63	27.9
	MRCI	1545.009 24	1.956	29.5	455.8	0.42	2.13/2.48	57.5
	MRCI+Q	1545.043 9	1.943	29.6			/2.42	63.6
13 $^3\Delta$	CASSCF	1544.589 13	1.931	8.33	613.7	0.43	2.28/2.68	41.4
	MRCI	1545.007 39	1.785	28.7	747.0	0.32	2.01/3.41	58.7
	MRCI+Q	1545.048 0	1.769	32.2			/3.51	61.0
14 $^5\Sigma^+$	CASSCF	1544.610 69	2.053	19.5	499.5	0.48	2.54/2.54	27.8
	MRCI	1545.006 85	1.990	27.4	466.7	0.42	2.11/2.39	59.0
	MRCI+Q	1545.040 9	1.988	27.3			/2.37	65.4
15 $^5\Phi$	CASSCF	1544.605 10	2.065	16.9	492.7	0.47	2.79/2.82	31.4
	MRCI	1545.003 37	2.006	25.7	476.6	0.42	2.51/2.85	61.2
	MRCI+Q	1545.038 4	2.004	26.1	462.6		/2.83	67.0
16 $^5\Delta$	CASSCF	1544.590 83	1.968	9.58	569.9	0.44	2.20/2.40	40.3
	MRCI	1544.999 40	1.860	23.8	828	0.33	1.98/3.53	63.7
	MRCI+Q	1545.037 2	1.851	25.7	917		/3.78	67.8
17 $^1\Sigma^+$	MRCI	1544.988 68	1.889	16.9	721.3	0.20	1.51/1.83	70.4
	MRCI+Q	1545.032 8	1.884	22.8			/1.74	70.5
	Expt. ^{f,g}		1.647 6					62.18
18 $^1\Delta$	MRCI	1544.981 29	1.861	12.2	606	0.18	0.69/0.56	75.1

TABLE I. (Continued.)

State	Method ^a	$-E$	r_e	D_e	ω_e	q_{Ni}	$\langle\mu\rangle/\mu_{\text{FF}}^b$	T_e
	MRCI+Q	1545.025 0	1.843	17.8			/0.27	75.4

^aInternally contracted MRCI and C-MRCI. +Q and +DKH2 refer to the multireference Davidson correction and to second order Douglas-Kroll-Hess relativistic corrections, respectively. 4Z basis set for states $3^3\Pi$ and above.

^b $\langle\mu\rangle$ obtained as an expectation value and μ_{FF} by the finite-field approach; the field strength is ± 0.0001 a.u.

^cThe semicore $3s^2 3p^6$ electrons of Ni are included in the MRCI.

^dReference 11; C-MRCI/[8s6p4d1f/Ni/cc-pVTZ/c]+Darwin+mass-velocity corrections.

^eReference 3, r_0 value.

^fReference 4.

^g[21.7] $\Omega=0^+$ state, r_0 value.

For the first three states $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$ core-valence correlation effects of the Ni $3s^2 3p^6$ electrons and DKH2 scalar relativistic effects in two bases, (4Z, C5Z) and (5Z-DK, C5Z-DK), have also been considered.

Table II presents leading equilibrium MRCI configurations, atomic Mulliken populations, and valence-bond-Lewis (vbL) diagrams indicating graphically the bonding character of every state. Figures 1–3 display the potential energy curves of seven singlets, seven triplets, and five quintets, respectively, calculated at the MRCI/4Z level and spanning an energy range of 3.3 eV. The inset of Fig. 1 shows the relative energies of all NiC states studied. We analyze first the singlets, then the triplets followed by the quintets.

A. Singlets ($X^1\Sigma^+$, $A^1\Pi$, $6^1\Phi$, $8^1\Pi$, $10^1\Delta$, $17^1\Sigma^+$, and $18^1\Delta$)

$X^1\Sigma^+$. The ground state of NiC is of $^1\Sigma^+$ symmetry, well separated from the first excited state $a^3\Pi$, located some 25 kcal/mol higher (see Fig. 1). It correlates to the ground state atoms $\text{Ni}(^3F; M=0)+\text{C}(^3P; M=0)$ maintaining this character up to equilibrium. The leading configuration and the Mulliken atomic distributions point clearly to a $2\pi+\sigma$ triple bond, as depicted in the vbL diagram of Table II. About $1e^-$ is transferred from the $4s4p3d_{z^2}$ -Ni hybrid to the empty $2p_z$ orbital of the C atom, whereas $\sim 0.8e^-$ are moving back to the metal through the π system.

It has been reported that the experimental dissociation energy of the $X^1\Sigma^+$ state of NiC is $D_e \geq 78.2$ kcal/mol.⁴ Recently, Rao *et al.*²³ by reevaluating the experimental data of Brugh and Morse⁴ obtained $D_0=79.6$ kcal/mol. At the highest level of theory, C-MRCI+DKH2(+Q)/C5Z, we get $D_e=84.0(94.2)$ kcal/mol; correcting this value for zero point energy (ZPE)($\cong \omega_e/2$)+BSSE ($=0.40$ kcal/mol), we obtain $D_0=82.3(91)$ kcal/mol. Because the Davidson-corrected (+Q) D value is significantly larger than the uncorrected one and the same is observed at all correlated levels of theory, MR-averaged pair functional²⁴ (MRACPF) and coupled-cluster [RCCSD(T)] valence calculations were also performed for the $X^1\Sigma^+$ state. MRACPF and RCCSD(T)/5Z D_e values are 94.0 and 99.5 kcal/mol, respectively. Note that the MRACPF value $D_e=94.1$ kcal/mol is identical to the MRCI+Q/5Z number (Table I). Taking into account the MRACPF results and that the multireference character of the system ($|C_0|^2=0.75$, Table II) erodes the reliability of the coupled-cluster calculation (T_1 diagnostic 0.0883), our sug-

gested value for the dissociation energy is $D_0=91$ kcal/mol. Also, our “best” interatomic distance 1.621(1.62) Å can be considered in good agreement with the experimental $r_e=1.62729$ Å.⁴ No experimental dipole moment is available, but we believe that the finite field μ_{FF} value of 2.20–2.30 D obtained at all levels of theory should be close to the true number. The corresponding D_e and μ values obtained recently by Borin¹⁰ differ substantially from the present ones being 68.7 kcal/mol and 1.266 D. Moreover, Shim and Gringerich⁷ and Borin¹⁰ report that the *in situ* atoms in the equilibrium are $\text{Ni}^+(a^4F)+\text{C}(^4S)$ contrary to our suggestion $\text{Ni}(a^3F)+\text{C}(^3P)$. We interpret the bond in a different way because, first, our results are not indicative of an ionic character of that extent and, second, the fragments $\text{Ni}^+(a^4F)+\text{C}(^4S)$ are lying much higher above the $\text{Ni}^+(a^3F)+\text{C}(^3P)$ asymptote: $\text{IE}[\text{Ni}^+(a^2D) \leftarrow \text{Ni}(a^3F)] + T_e(\text{Ni}; a^4F \leftarrow a^2D) - \text{EA}[\text{C}(^4S) \leftarrow \text{C}(^3P)] = 7.6398$ (Ref. 22) + 1.0851 (Ref. 22) – 1.2629 (Ref. 25) eV = 7.462 eV (=172.08 kcal/mol).

Finally, it should be mentioned that our results at the highest level of theory C-MRCI+DKH2(+Q) are in very good agreement with the “plain” MRCI(+Q)/4Z results and the same is true for the next two states, $a^3\Pi$ and $A^1\Pi$ (*vide infra*).

The $A^1\Pi$ is the second excited state, certainly more than 30 kcal/mol above the $X^1\Sigma^+$ one. It correlates to $\text{Ni}(a^3F; M=\pm 1)+\text{C}(^3P; M=0)$, but around 3.4 bohrs it interacts with the $8^1\Pi$ thus changing its equilibrium character to $\text{Ni}(a^3D, M=\pm 1)+\text{C}(^3P; M=0)$ (Fig. 1). Recall that the Ni atomic states $a^3F(4s^2 3d^8)$ and $a^3D(4s^1 3d^9)$ are in essence degenerate. This is one of the three states (the other two are $X^1\Sigma^+$ and $a^3\Pi$) where very extensive calculations are performed in the present work including valence-core ($3s^2 3p^6$) correlation and scalar relativistic corrections (C-MRCI+DKH2/C5Z), with the purpose to obtain accurately enough results as well as to gauge our “simpler” MRCI/4Z calculations for the rest of the 16 states examined.

A double bond of (σ, π) character is observed; the result of about $0.5e^-$ transfer from the $3d_{z^2}$ atomic orbital of Ni to the empty $2p_z$ ($M=0$) orbital of C, with a back transfer of $0.3e^-$ through the π system from C to Ni (Table II). At the highest level of theory C-MRCI+DKH2/C5Z(+Q) the binding energy is $D_e=48.9(56.0)$ kcal/mol, with the +Q result being corroborated at the C-MRACPF+DKH2/5Z level. Correcting for ZPE and BSSE, the suggested dissociation energy is $D_0=54$ kcal/mol at $r_e=1.61$ – 1.62 Å. We can

TABLE II. MRCI/4Z leading configurations, atomic Mulliken populations, and valence-bond-lewis diagrams (vBL) for 19 states of the NiC molecule.

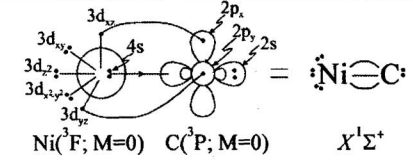
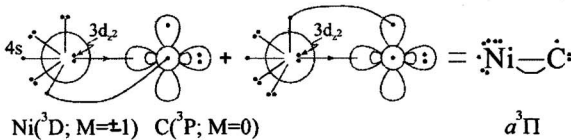
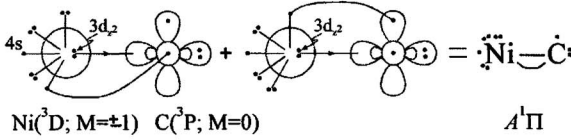
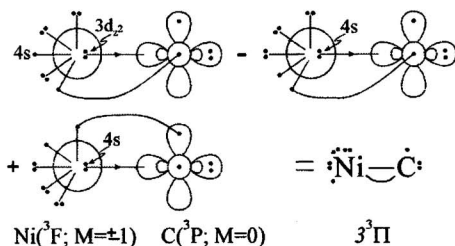
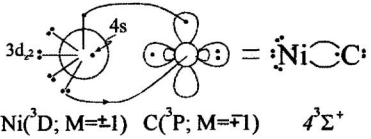
State ^a	Leading Configurations	Population Analysis	vBL
$X^1\Sigma^+$	$0.85 1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 1\delta_+^2 1\delta_-^2\rangle_{A_1}$	$4s^{1.12} 4p_z^{0.14} 3d_z^{1.71} 3d_{xz}^{1.41} 4p_x^{0.03} 3d_{yz}^{1.41} 4p_y^{0.03} 3d_{x^2-y^2}^{1.98} 3d_{xy}^{1.98}$ $2s^{1.77} 2p_z^{1.19} 2p_x^{0.56} 2p_y^{0.56}$	 Ni(³ F; M=0) C(³ P; M=0) $X^1\Sigma^+$
$a^3\Pi$	$1/\sqrt{2} \times 0.85 1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 (2\pi_x^1 + 2\pi_y^1) 1\delta_+^2 1\delta_-^2\rangle_{B_1+B_2}$	$4s^{0.93} 4p_z^{0.16} 3d_z^{1.46} 3d_{xz}^{1.59} 4p_x^{0.06} 3d_{yz}^{1.59} 4p_y^{0.06} 3d_{x^2-y^2}^{1.98} 3d_{xy}^{1.98}$ $2s^{1.74} 2p_z^{0.70} 2p_x^{0.84} 2p_y^{0.84}$	 Ni(³ D; M=±1) C(³ P; M=0) $a^3\Pi$
$A^1\Pi$	$1/\sqrt{2} \times 0.80 1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 (2\pi_x^1 + 2\pi_y^1) 1\delta_+^2 1\delta_-^2\rangle_{B_1+B_2}$	$4s^{1.00} 4p_z^{0.22} 3d_z^{1.37} 3d_{xz}^{1.61} 4p_x^{0.04} 3d_{yz}^{1.61} 4p_y^{0.04} 3d_{x^2-y^2}^{1.95} 3d_{xy}^{1.95}$ $2s^{1.75} 2p_z^{0.70} 2p_x^{0.84} 2p_y^{0.84}$	 Ni(³ D; M=±1) C(³ P; M=0) $A^1\Pi$
$3^3\Pi$	$(1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 2\pi_x^1)[0.46(1\pi_y^2) - 0.22(1\pi_y^1 2\pi_y^1)] \times (1\delta_+^2 1\delta_-^2) + 0.44(1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2) (1\pi_y^2 2\pi_y^1 1\delta_+^2 1\delta_-^2 - 2\pi_x^1 1\pi_y^2 1\delta_+^1 1\delta_-^2)\rangle_{B_1}$	$4s^{1.12} 4p_z^{0.17} 3d_z^{1.63} 3d_{xz}^{1.65} 4p_x^{0.05} 3d_{yz}^{1.65} 4p_y^{0.05} 3d_{x^2-y^2}^{1.72} 3d_{xy}^{1.72}$ $2s^{1.73} 2p_z^{0.85} 2p_x^{0.79} 2p_y^{0.79}$	 Ni(³ F; M=±1) C(³ P; M=0) $3^3\Pi$
$4^3\Sigma^+$	$ 1\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 [0.78(1\pi_x^2 1\pi_y^2) - 0.21(2\pi_x^2 1\pi_y^2 + 1\pi_x^2 2\pi_y^2)] 1\delta_+^2 1\delta_-^2\rangle_{A_1}$	$4s^{1.12} 4p_z^{0.31} 3d_z^{1.82} 3d_{xz}^{1.30} 4p_x^{0.03} 3d_{yz}^{1.30} 4p_y^{0.03} 3d_{x^2-y^2}^{1.97} 3d_{xy}^{1.97}$ $2s^{1.71} 2p_z^{0.99} 2p_x^{0.67} 2p_y^{0.67}$	 Ni(³ D; M=±1) C(³ P; M=±1) $4^3\Sigma^+$

TABLE II. (Continued.)

$5^3\Phi$	$0.55 \left \sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 (2\pi_x^1 1\delta_x^+ 1\delta_y^+ 1\delta_z^+ - 2\pi_y^1 1\delta_x^+ 1\delta_z^+) \right\rangle_{B_1}$	$4s^{1.24} 4p_z^{0.20} 3d_{z^2}^{1.81} 3d_{xz}^{0.05} 3d_{yz}^{1.68} 4p_x^{0.05} 3d_{x^2-y^2}^{1.50} 3d_{xy}^{1.50}$ $2s^{1.77} 2p_z^{0.91} 2p_x^{0.76} 2p_y^{0.76}$		$Ni(3F; M=\pm 3) \quad C(3P; M=0) \quad 5^3\Phi$
$6^1\Phi$	$0.55 \left \sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 (2\pi_x^1 1\delta_x^+ 1\delta_y^+ 1\delta_z^+ + 2\pi_y^1 1\delta_x^+ 1\delta_z^+) \right\rangle_{B_1}$	$4s^{1.24} 4p_z^{0.22} 3d_{z^2}^{1.84} 3d_{xz}^{0.05} 3d_{yz}^{1.68} 4p_x^{0.05} 3d_{x^2-y^2}^{1.50} 3d_{xy}^{1.50}$ $2s^{1.77} 2p_z^{0.86} 2p_x^{0.80} 2p_y^{0.80}$		$Ni(3F; M=\pm 3) \quad C(3P; M=0) \quad 6^1\Phi$
$7^3\Delta$	$1/\sqrt{2} \times 0.89 \left \sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 1\pi_y^2 2\pi_z^1 \right\rangle_{A_1+A_2}$ $\left(1\delta_x^+ 1\delta_y^+ + 1\delta_z^+ 1\delta_x^- \right) \Big _{A_1+A_2}$	$4s^{0.94} 4p_z^{0.15} 3d_{z^2}^{1.53} 3d_{xz}^{1.91} 4p_x^{0.11} 3d_{yz}^{1.91} 4p_y^{0.11} 3d_{x^2-y^2}^{1.50} 3d_{xy}^{1.50}$ $2s^{1.72} 2p_z^{0.62} 2p_x^{0.96} 2p_y^{0.96}$		$Ni(3D; M=\pm 2) \quad C(3P; M=0) \quad 7^3\Delta$
$8^1\Pi$	$0.52 \left \sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 1\pi_y^2 1\delta_x^+ 1\delta_z^- \right\rangle +$ $+ 0.43 \left \sigma^2 2\sigma^2 3\sigma^2 \left(1\pi_x^2 1\pi_y^2 2\pi_z^1 1\delta_x^+ 1\delta_z^- - 1\pi_x^2 2\pi_y^1 1\pi_z^2 1\delta_x^+ 1\delta_z^- \right) \right\rangle_{B_1}$	$4s^{1.12} 4p_z^{0.17} 3d_{z^2}^{1.58} 3d_{xz}^{1.69} 4p_x^{0.04} 3d_{yz}^{1.69} 4p_y^{0.04} 3d_{x^2-y^2}^{1.73} 3d_{xy}^{1.73}$ $2s^{1.76} 2p_z^{0.84} 2p_x^{0.77} 2p_y^{0.77}$		$Ni(3F; M=\pm 1) \quad C(3P; M=0) \quad 8^1\Pi$
$9^3\Delta_G$	$\left\{ 0.69 \left(1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 1\pi_y^2 2\pi_z^1 \right) + \right.$ $\left. \left(\sigma^2 2\sigma^2 3\sigma^2 \right) \left[0.44 \left(1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 \right) \right. \right.$ $\left. \left. + 0.31 \left(1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_z^1 \right) \right] \right\} \left(1\delta_x^+ 1\delta_z^- \right) \Big _{A_2}$	$4s^{0.99} 4p_z^{0.14} 3d_{z^2}^{1.47} 3d_{xz}^{1.95} 4p_x^{0.09} 3d_{yz}^{1.95} 4p_y^{0.09} 3d_{x^2-y^2}^{1.00} 3d_{xy}^{1.99}$ $2s^{1.67} 2p_z^{0.69} 2p_x^{0.95} 2p_y^{0.95}$		$Ni(3D; M=\pm 2) \quad C(3P; M=0) \quad 9^3\Delta_G$
$9^3\Delta_L$	$\left\{ \left[0.64 \left(1\sigma^2 2\sigma^2 3\sigma^2 \right) - 0.25 \left(1\sigma^2 3\sigma^2 4\sigma^2 \right) \right] \right.$ $\left. \left(1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 \right) + \left[0.46 \left(1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 2\pi_y^1 1\pi_z^2 \right) \right. \right.$ $\left. \left. 2\pi_z^1 \right] + 0.23 \left(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 \right) \right\}$ $\left(1\delta_x^+ 1\delta_z^- \right) - 0.20 \left(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi_x^2 2\pi_y^1 1\pi_z^2 2\pi_x^1 \right.$ $\left. \left. 1\delta_x^+ 1\delta_z^- \right) \right\} \Big _{A_2}$	$4s^{1.10} 4p_z^{0.26} 3d_{z^2}^{1.10} 3d_{xz}^{2.00} 4p_x^{0.05} 3d_{yz}^{2.00} 4p_y^{0.05} 3d_{x^2-y^2}^{1.00} 3d_{xy}^{1.99}$ $2s^{1.76} 2p_z^{0.74} 2p_x^{0.95} 2p_y^{0.95}$		$Ni(3F; M=\pm 2) \quad C(3P; M=0) \quad 9^3\Delta_L$

TABLE II. (Continued.)

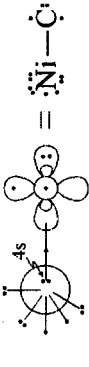
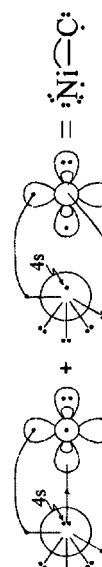
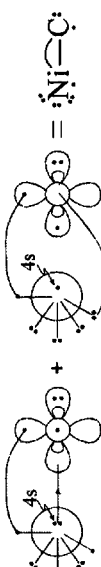
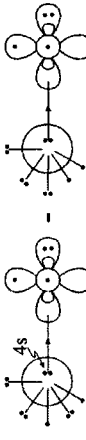
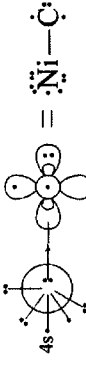
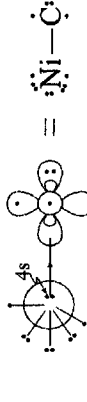
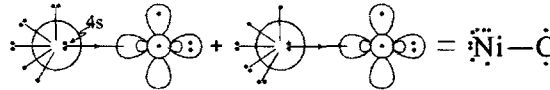
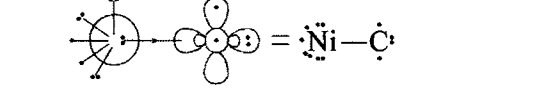
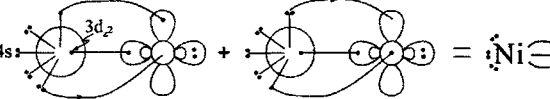
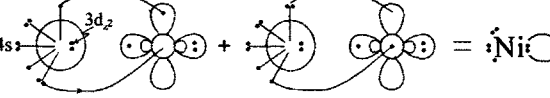
$1^1\theta^1\Delta$	$\begin{aligned} & [0.80(\sigma^2 2\sigma^2 3\sigma^1) - 0.32(\sigma^2 3\sigma^1 4\sigma^2) - \\ & + 0.23(\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1) - 0.19(\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1)] \\ & (1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^+) - 0.28(\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1 \\ & 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^+) \Bigg\} A_2 \end{aligned}$	$\begin{aligned} & 4s^{1.10} 4p_z^{0.26} 3d_{z^2}^{1.10} 3d_{xz}^{2.00} 4p_x^{0.04} 3d_{yz}^{2.00} 4p_y^{0.04} 3d_{x^2-y^2}^{1.00} 3d_{xy}^{1.99} \\ & 2s^{1.71} 2p_z^{0.73} 2p_x^{0.95} 2p_y^{0.95} \end{aligned}$	 <p>Ni(3F; M=2) C(3P; M=0) $1^1\theta^1\Delta$</p>	 <p>Ni(3F, 3D on the crossing) C(3P) $1^1\Sigma^+$</p>
$1^1\Sigma^+$	$\begin{aligned} & \sigma^2 2\sigma^2 3\sigma^1 4\sigma^1 [0.43(1\pi_x^2 1\pi_y^2) + 0.29(1\pi_x^2 1\pi_y^2 2\pi_y^1 \\ & + 1\pi_x^1 2\pi_x^1 1\pi_y^2) + 0.21(1\pi_x^1 2\pi_x^1 1\pi_y^2 2\pi_y^1)] 1\delta_x^+ 1\delta_y^2 \\ & + 0.31 \sigma^2 2\sigma^2 3\sigma^2 (1\pi_x^2 1\pi_y^2 2\pi_y^1 + 1\pi_x^1 2\pi_x^1 1\pi_y^2) \\ & 1\delta_x^+ 1\delta_y^2 \Bigg\} A_1 \end{aligned}$	$\begin{aligned} & 4s^{1.15} 4p_z^{0.29} 3d_{z^2}^{1.83} 3d_{xz}^{1.26} 4p_x^{0.04} 3d_{yz}^{1.26} 4p_y^{0.04} 3d_{x^2-y^2}^{1.94} 3d_{xy}^{1.94} \\ & 2s^{1.73} 2p_z^{0.86} 2p_x^{0.75} 2p_y^{0.75} \end{aligned}$	 <p>Ni(3F, 3D on the crossing) C(3P) $1^1\Sigma^+$</p>	
$1^2\Pi$	$\begin{aligned} & [0.40(\sigma^2 2\sigma^1 3\sigma^2) - 0.28(\sigma^2 2\sigma^2 3\sigma^1) - \\ & - 0.19(\sigma^2 2\sigma^1 4\sigma^2)] (1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) - \\ & - 0.33(\sigma^2 2\sigma^2 3\sigma^2 (1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) + \\ & + 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) + 0.23(\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1) \\ & (1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 + 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1)] \delta_x^+ 1\delta_y^2 \Bigg\} B_1 \end{aligned}$	$\begin{aligned} & 4s^{1.12} 4p_z^{0.28} 3d_{z^2}^{1.49} 3d_{xz}^{1.52} 4p_x^{0.05} 3d_{yz}^{1.52} 4p_y^{0.05} 3d_{x^2-y^2}^{1.76} 3d_{xy}^{1.76} \\ & 2s^{1.75} 2p_z^{0.79} 2p_x^{0.93} 2p_y^{0.93} \end{aligned}$	 <p>Ni(3F; M=1) C(3P; M=0) $1^2\Pi$</p>	
$1^3\Sigma$	$\begin{aligned} & [0.69(\sigma^2 2\sigma^2 3\sigma^1) - 0.30(\sigma^2 2\sigma^1 3\sigma^1 4\sigma^1)] \\ & (1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) - 0.23(\sigma^2 2\sigma^1 3\sigma^2 \\ & 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) \Bigg\} A_2 \end{aligned}$	$\begin{aligned} & 4s^{1.10} 4p_z^{0.21} 3d_{z^2}^{1.30} 3d_{xz}^{1.97} 4p_x^{0.06} 3d_{yz}^{1.97} 4p_y^{0.06} 3d_{x^2-y^2}^{1.00} 3d_{xy}^{1.99} \\ & 2s^{1.65} 2p_z^{0.72} 2p_x^{0.95} 2p_y^{0.95} \end{aligned}$	 <p>Ni(3D; M=2) C(3P; M=0) $1^3\Sigma$</p>	
$1^4\Sigma^+$	$\begin{aligned} & [0.61(\sigma^2 2\sigma^2 3\sigma^2) - 0.27(\sigma^2 2\sigma^2 4\sigma^2)] \\ & (1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) + (\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1) \\ & [0.31(1\pi_x^2 1\pi_y^2 2\pi_y^1 + 1\pi_x^1 2\pi_x^1 1\pi_y^2) + 0.21(1\pi_x^1 2\pi_x^1 \\ & 1\pi_y^2 2\pi_y^1) + 0.19(1\pi_x^1 2\pi_x^1 1\pi_y^2 2\pi_y^1)] (1\delta_x^2 1\delta_y^2) + \\ & 0.23(\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_x^+ 1\delta_y^2) \Bigg\} A_1 \end{aligned}$	$\begin{aligned} & 4s^{1.15} 4p_z^{0.29} 3d_{z^2}^{1.97} 3d_{xz}^{1.16} 4p_x^{0.05} 3d_{yz}^{1.16} 4p_y^{0.05} 3d_{x^2-y^2}^{1.87} 3d_{xy}^{1.87} \\ & 2s^{1.76} 2p_z^{0.79} 2p_x^{0.92} 2p_y^{0.92} \end{aligned}$	 <p>Ni(3F; M=0) C(3P; M=0) $1^4\Sigma^+$</p>	

TABLE II. (Continued.)

$15^5\Phi$	$\left[0.54(\sigma^2 2\sigma^2 3\sigma^2) - 0.21(\sigma^2 2\sigma^2 4\sigma^2)\right] \left[1\pi_x^1 2\pi_x^1\right. \\ \left.1\pi_y^2 2\pi_y^1 1\delta_+^2 1\delta_-^1 - 1\pi_x^2 2\pi_x^1 1\pi_y^1 2\pi_y^1 1\delta_+^1 1\delta_-^2\right] \\ + (\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1) \left[0.23(1\pi_x^1 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_+^2 1\delta_-^1) \right. \\ \left. - 0.21(1\pi_x^2 2\pi_x^1 1\pi_y^1 2\pi_y^1 + 1\pi_x^2 2\pi_x^1 1\pi_y^1 2\pi_y^1) \right. \\ \left. (1\delta_+^1 1\delta_-^2)\right]_{B_1}$	$4s^{1.21} 4p_z^{0.26} 3d_{z^2}^{1.96} 3d_{xz}^{1.52} 4p_x^{0.05} 3d_{yz}^{1.52} 4p_y^{0.05} 3d_{x^2-y^2}^{1.50} 3d_{xy}^{1.50} \\ 2s^{1.78} 2p_z^{0.75} 2p_x^{0.92} 2p_y^{0.92}$	 <p style="text-align: center;">Ni(3D; $M=\pm 3$) C(3P; $M=0$) $15^5\Phi$</p>
$16^5\Delta$	$\left[0.60(\sigma^2 2\sigma^2 3\sigma^1) - 0.47(\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1) + \right. \\ \left. + 0.40(\sigma^2 2\sigma^1 3\sigma^2) - 0.25(\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1)\right] \times \\ \left. 1\pi_x^2 2\pi_x^1 1\pi_y^2 2\pi_y^1 1\delta_+^1 1\delta_-^2\right\}_{A_2}$	$4s^{1.18} 4p_z^{0.22} 3d_{z^2}^{1.18} 3d_{xz}^{1.98} 4p_x^{0.06} 3d_{yz}^{1.98} 4p_y^{0.06} 3d_{x^2-y^2}^{1.00} 3d_{xy}^{1.99} \\ 2s^{1.63} 2p_z^{0.77} 2p_x^{0.95} 2p_y^{0.95}$	 <p style="text-align: center;">Ni(3F3D; crossing) C(3P; $M=0$) $16^5\Delta$</p>
$17^1\Sigma^+$	$\left[0.43(\sigma^2 2\sigma^2 3\sigma^2) - 0.31(\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1) + \right. \\ \left. + 0.26(\sigma^2 2\sigma^1 3\sigma^2 4\sigma^1)\right] \left(1\pi_x^2 1\pi_y^2 1\delta_+^2 1\delta_-^2\right) + \\ + 0.21(\sigma^2 2\sigma^2 3\sigma^2) \left(1\pi_x^1 2\pi_x^1 1\pi_y^2 + 1\pi_x^2 1\pi_y^1 2\pi_y^1 \right. \\ \left. - 1\pi_x^1 2\pi_x^1 1\pi_y^1 2\pi_y^1\right) \left(1\delta_+^2 1\delta_-^2\right)\}_{A_1}$	$4s^{1.25} 4p_z^{0.23} 3d_{z^2}^{1.41} 3d_{xz}^{1.53} 4p_x^{0.03} 3d_{yz}^{1.53} 4p_y^{0.03} 3d_{x^2-y^2}^{1.89} 3d_{xy}^{1.89} \\ 2s^{1.63} 2p_z^{0.77} 2p_x^{0.95} 2p_y^{0.95}$	 <p style="text-align: center;">Ni(3F; $M=\pm 1$) C(3P; $M=\mp 1$) $17^1\Sigma^+(2)$</p>
$18^1\Delta$	$\left[(\sigma^2 2\sigma^2 3\sigma^1 4\sigma^1) \left(0.63(1\pi_x^2 1\pi_y^2) + 0.26(1\pi_x^2 1\pi_y^1 2\pi_y^1 \right. \right. \\ \left. \left. + 1\pi_x^1 2\pi_x^1 1\pi_y^2)\right) \left(1\delta_+^1 1\delta_-^2\right) - 0.21(\sigma^2 2\sigma^2 3\sigma^2) \times \right. \\ \left. (1\pi_x^1 2\pi_x^1 1\pi_y^2 - 1\pi_x^2 1\pi_y^1 2\pi_y^1)\right] \left(1\delta_+^2 1\delta_-^2\right)\}_{A_1}$	$4s^{1.33} 4p_z^{0.30} 3d_{z^2}^{1.81} 3d_{xz}^{1.56} 4p_x^{0.03} 3d_{yz}^{1.56} 4p_y^{0.03} 3d_{x^2-y^2}^{1.20} 3d_{xy}^{1.99} \\ 2s^{1.78} 2p_z^{1.46} 2p_x^{0.45} 2p_y^{0.45}$	 <p style="text-align: center;">Ni(3F; $M=\pm 1$) C(3P; $M=\mp 1$) $18^1\Delta(2)$</p>

³G refers to the global minimum and L refers to the local minimum.

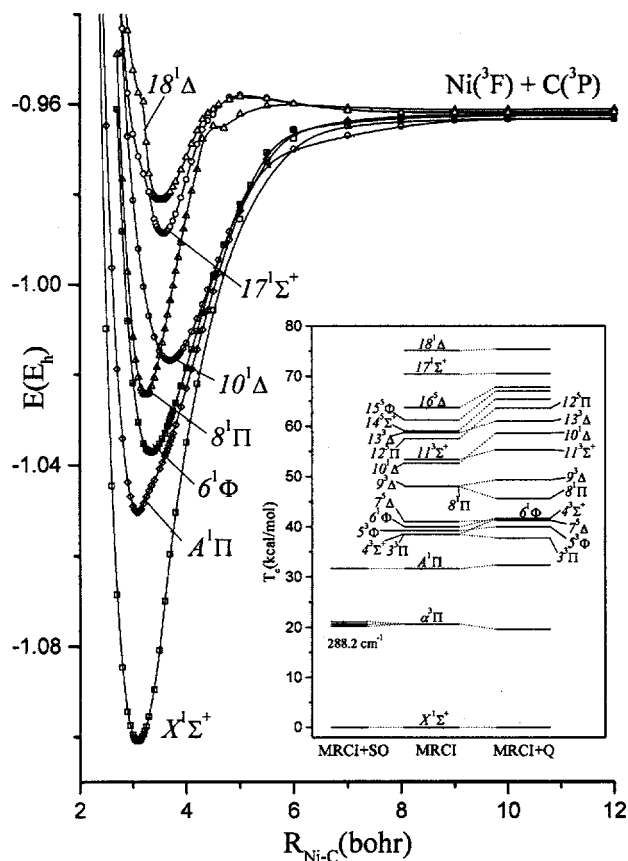


FIG. 1. MRCI/4Z potential energy curves of the NiC singlets. All energies shifted by $+1544.0 E_h$. Inset: MRCI and MRCI+Q relative energy levels of 19 NiC states including SO splittings for the $a^3\Pi$ state.

also claim with confidence that the $A^1\Pi \leftarrow X^1\Sigma^+$ energy separation is $T_e=37$ kcal/mol (37.8 at the C-MRACPF+DKH2/C5Z level), and the finite field dipole moment is $\mu_{FF}=2.1$ D. The corresponding C-MRCI results of Borin¹⁰ are $D_e=42.0$ kcal/mol, $r_e=1.773$ Å, $T_e=27.0$ kcal/mol, and $\mu=1.822$ D, again differing significantly from the present ones.

As in the $X^1\Sigma^+$ state the plain MRCI and/or MRCI+Q/4Z results could be considered in relatively good agreement with those at the highest level of theory.

We now briefly examine the rest of the singlets studied, namely, $6^1\Phi$, $8^1\Pi$, $10^1\Delta$, $17^1\Sigma^+$, and $18^1\Delta$. Their MRCI/4Z potential curves are shown in Fig. 1 and their bonding character and atomic Mulliken distributions in Table II. With the exception of the $8^1\Pi$ state which suffers an avoided crossing around 4.0 bohr with another (not calculated) $^1\Pi$ stemming from the a^3D atomic state of Ni and at the 3.4 bohr with the $a^1\Pi$ (*vide supra*), the rest of the states maintain their character from infinity to equilibrium. The $6^1\Phi$ and $8^1\Pi$ interact attractively through a double (σ, π) bond, the $10^1\Delta$ with a single σ bond, the $17^1\Sigma^+$ with triple ($\sigma, 2\pi$) bond, and the $18^1\Delta$ state shows a double (π_x, π_y) bond character. The MRCI(MRCI+Q)/4Z dissociation energies and bond distances are $D_e=46.9(51.5)$, $39.8(47.9)$, $33.6(34.0)$, $16.9(22.8)$, and $12.2(17.8)$ kcal/mol and $r_e=1.766(1.737)$, $1.713(1.712)$, $1.955(1.945)$, $1.889(1.884)$, and $1.861(1.843)$ Å, respectively. A total Mulliken charge

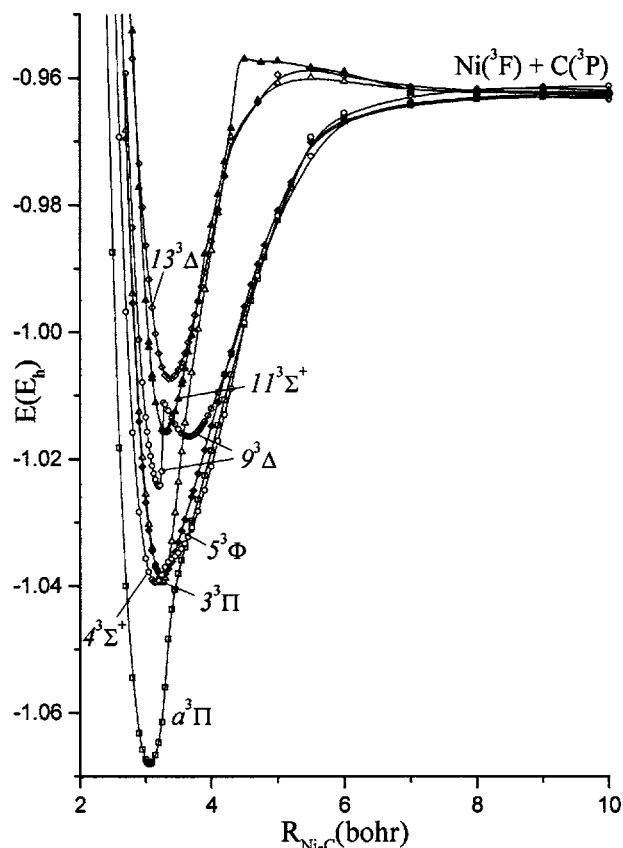


FIG. 2. MRCI/4Z potential energy curves of the NiC triplets. All energies shifted by $+1544.0 E_h$.

transfer of $0.2e^- - 0.4e^-$ from Ni to C is also observed for all five singlets.

For the $6^1\Phi$ and $10^1\Delta$ states, the C-MRCI D_e and r_e values of Borin and Macedo¹¹ are 39.9 and 27.9 kcal/mol and 1.784 and 1.992 Å, respectively, whereas their corresponding T_e values ($10^1\Delta, 6^1\Phi \leftarrow X^1\Sigma^+$) are more than 11 kcal/mol smaller from the present ones at the MRCI/4Z level.

Brugh and Morse observed an electronic state tagged $[21.7]\Omega=0^+$, with $T_0=62.19$ kcal/mol and $r_0=1.6476$ Å.⁴ Our $17^1\Sigma^+$ has $D_e=16.9(22.8)$ kcal/mol, $r_e=1.889(1.884)$ Å, and $T_e=70.4(70.5)$ kcal/mol at MRCI(MRCI+Q)/4Z level of theory, not in agreement with the experimental results of the $[21.7]\Omega=0^+$ state.

B. Triplets ($a^3\Pi$, $3^3\Pi$, $4^3\Sigma^+$, $5^3\Phi$, $9^3\Delta$, $11^3\Sigma^+$, and $13^3\Delta$)

$a^3\Pi$. This is the first excited state of NiC located 25.0(24.5) kcal/mol above the $X^1\Sigma^+$ one at the C-MRCI+DKH2/C5Z(+Q) level of theory. It correlates to $Ni(a^3F; M=\pm 1)+C(^3P; M=0)$ but near 3.4 bohrs suffers an avoided crossing with the $3^3\Pi$ state; therefore, the *in situ* equilibrium character of Ni becomes $a^3D(M=\pm 1)$ (Fig. 2). The two atoms are held together by a double (σ, π) bond, the result of $0.4e^-$ transfer through the σ system from the $3d_{z^2}$ orbital to the empty $2p_z$ of the C atom, and $0.2e^-$ moving back via the π system from C to Ni.

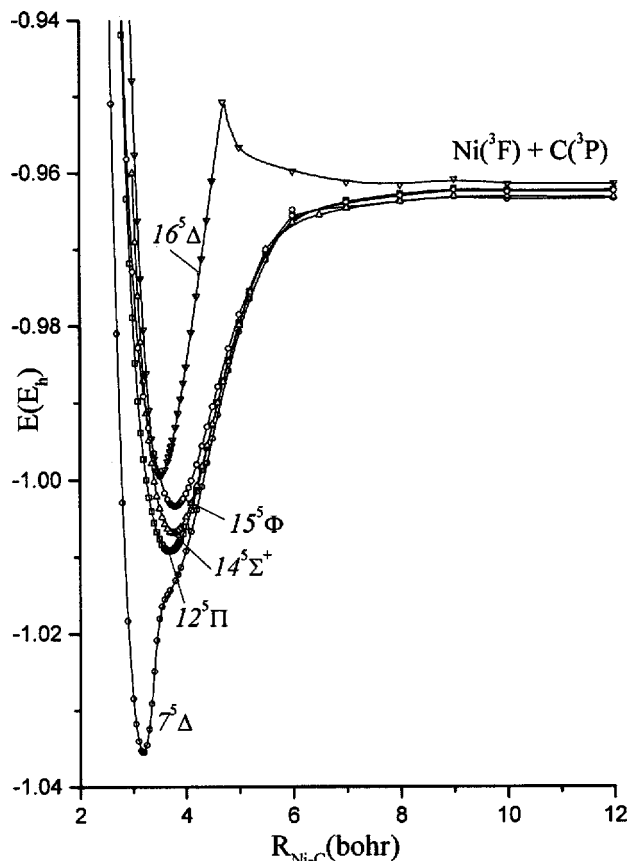


FIG. 3. MRCI/4Z potential energy curves of the NiC quintets. All energies shifted by $+1544.0 E_h$.

At the C-MRCI+DKH2+Q/C5Z level, $D_e = 68.4$ kcal/mol at $r_e = 1.598$ Å. Correcting this value for ZPE and BSSE the recommended dissociation energy is $D_0 = 67$ kcal/mol; a 2 kcal/mol higher D_0 is obtained at the ACPF level. At all correlated levels the finite field dipole moment $\mu_{FF} = 3.3$ D. Although the C-MRCI r_e and $T_e(a^3\Pi \leftarrow X^1\Sigma^+)$ values of Borin and Macedo¹¹ are similar to ours, their D_e value is by 22 kcal/mol smaller. Finally, the spin-orbit splitting calculated at the MRCI/4Z level gives rise to three components $a^3\Pi_2$, $a^3\Pi_1$, and $a^3\Pi_0$ separated by 144 cm^{-1} .

The next three triplets $3^3\Pi$, $4^3\Sigma^+$, and $5^3\Phi$ are essentially degenerate at the MRCI/4Z level, but they are well separated and reordered at the +Q level (Table I and inset of Fig. 1). The $3^3\Pi$ state from infinity to equilibrium suffers two avoided crossings, one at 4.5 bohr with another (not calculated) $^3\Pi$ state correlating to Ni(a^3D) and a second one near 3.4 bohr with the previously described $a^3\Pi$ state. We are rather confident that the $3^3\Pi$ state is the third excited state of NiC and could also be tagged as $b^3\Pi$.

According to Table II these three triplets are double bonded with (σ, π) , (π, π) , and (σ, π) bonds and with very similar binding energies and interatomic distances.

The next three triplets $9^3\Delta$, $11^3\Sigma^+$, and $13^3\Delta$ are well separated at the MRCI/4Z level, maintaining also their order and splittings at the Davidson +Q correction level. The $9^3\Delta$ suffers a remarkable avoided crossing near 3.4 bohr with the $13^3\Delta$ state, thus showing two minima, a global (G) and a

local (L) one at $r_e = 1.696$ and 1.936 Å, respectively (Fig. 2). It is interesting that the corresponding C-MRCI $^3\Delta$ state PEC of Borin and Macedo¹¹ does not show this crossing, whereas their $r_e = 1.970$ Å points to the L minimum. The $11^3\Sigma^+$ also shows an avoided crossing near 4.4 bohr with another $^3\Sigma^+$ state stemming from the Ni a^3D term.

The 9, 11, and 13 triplets feature a single σ , a double (σ, π) , and a single σ bond, respectively, with a total Mulliken charge transfer from Ni to C of about $0.3e^-$ (Table II). Their MRCI(+Q)/4Z binding energies and bond distances are $D_e = 39.1$ (43.9), 34.0 (38.0), and 28.7(32.2) kcal/mol and $r_e = 1.696$ (1.693), 1.746(1.734), and 1.785(1.796) Å, respectively.

C. Quintets ($7^5\Delta$, $12^5\Pi$, $14^5\Sigma^+$, $15^5\Phi$, and $16^5\Delta$)

The MRCI potential energy curves of the quintets above are shown in Fig. 3, all correlating to Ni(a^3F)+C(3P ; $M=0$). All five states interact attractively through a single σ bond, the result of a strong electron transfer from the $4s^2$ orbital of Ni to the empty $2p_z$ ($M=0$) C orbital in four out of the five states; in the $7^5\Delta$ state the Ni $3d_{z^2}$ orbital is the cause of the σ -electron transfer to the empty $2p_z$ orbital of carbon (Table II). Because of the lack of back electron transfer, the π route is Pauli closed; all quintets show a larger Mulliken Ni-to-C charge transfer than the singlets or the triplets.

The lowest state of the quintet manifold, $7^5\Delta$, shows a strong avoided crossing near 3.5 bohr with the $16^5\Delta$; the latter has already suffered an intense avoided crossing at about 4.6 bohrs with a (not calculated) $^5\Delta$ state stemming from the Ni(a^3D ; $M=\pm 2$) term. The MRCI(+Q)/4Z r_e and D_e values of $7^5\Delta$ are 1.685(1.676) Å and 45.3(50.8) kcal/mol, respectively.

The next three states maintain their character from infinity to equilibrium and show a strong charge transfer from Ni to C atom of near $0.5e^-$ with similar binding energies (25–30 kcal/mol) and bond distances (1.96–2.00 Å).

IV. SUMMARY

The primary results of this work can be epitomized as follows.

The ground state of NiC is of $^1\Sigma^+$ symmetry with a triple bond character and a recommended binding energy $D_0 = 91$ kcal/mol; we remind that there is no accurate experimental dissociation energy. Our “best” interatomic distance $r_e = 1.621$ Å is in good agreement with the experimental value of 1.62729 Å.

In all 19 states studied (seven singlets, seven triplets, and five quintets), the Mulliken charge transfer from Ni to C ranges from $0.2e^-$ to $0.5e^-$, in accord to “chemical intuition.” In 16 out of the 19 states the *in situ* carbon atom finds itself in the $M=0$ orientation, thus enhancing the σ Ni-to-C charge transfer.

Judging from the first three states ($X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$) where scalar relativistic effects were taken into consideration through the second order Douglas-Kroll-Hess (DKH2) approach, relativistic effects are of some importance. Of course, this depends on the level of calculation and

the accuracy that one is after. For the $X^1\Sigma^+$ state the DKH2 correction amounts to a decrease of binding energy and bond distance by 1 kcal/mol and 0.025 Å, whereas the corresponding values for the $a^3\Pi$ and $A^1\Pi$ states are -4 kcal/mol and -0.01 to -0.005 Å.

Basis set superposition error (BSSE) corrections can be very sizable even for large basis set if, for instance, core-correlation effects are included but without specially “tuned” core functions. In the present case BSSE of 3.5 kcal/mol were calculated when including the $3s^23p^6$ semicore electrons of Ni in the CI procedure but without appropriate core functions. This number reduces to about 0.4 kcal/mol once core functions are added. Exactly the same effect was observed in the case of vanadium oxide (VO).²⁶

In accord with previous observations,^{2(g)} finite field dipole moments (μ_{FF}) can differ significantly from expectation value ones ($\langle\mu\rangle$), the former being usually larger. An extreme example in the present case is the μ_{FF} and $\langle\mu\rangle$ MRCI/4Z values of $9^3\Delta$ state, where $\mu_{FF}=4.57$ and $\langle\mu\rangle=2.73$ D. In addition, we have concluded that the MRCI level μ_{FF} is insensitive to the state averaged (SA) approach,^{2(g)} contrary to the case of CASSCF level; of course $\langle\mu\rangle=\mu_{FF}$ at the CASSCF level when the SA is not employed. In general μ_{FF} values should be trusted more than $\langle\mu\rangle$ ones; therefore, the dipole moment of the NiC $X^1\Sigma^+$ is 2.3 D.

Finally we hope that the results of the present work will prove useful to both experimentalists and theoreticians. Certainly, we cannot claim chemical accuracy (± 1 mE_h in D_e) even for the three lowest states $X^1\Sigma^+$, $a^3\Pi$, and $A^1\Pi$; for the rest of the states it is fair to judge our results as simply semiquantitative. Perhaps it is instructive to realize that despite the unquestionable progress in theoretical and computational chemistry in the last 25–30 years, even “small” diatomics like the present one can be proven very challenging computationally for a variety of reasons. In addition, the always present “interpretational” component is another problem, very difficult to be confronted effectively due to its intrinsic subjectiveness.

ACKNOWLEDGMENTS

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