

The electronic structure of the two lowest states of CuC

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State-of-the-art *ab initio* quantum mechanical methods and large basis sets are employed for the study of the electronic structure of the first two states of CuC, $4\Sigma^-$ and 2Π . A one-electron sigma bond state ($4\Sigma^-$) competes with a two-electron σ -bond state (2Π) for the ground state of the CuC system. The combined effects of core-valence correlation and relativity point to an X -state of 2Π symmetry with $D_e=51.9$ kcal/mol and $r_e=1.772$ Å. The $4\Sigma^-$ state is predicted to lie 2.1 kcal/mol higher at $r_e=1.787$ Å. © 2008 American Institute of Physics. [DOI: 10.1063/1.3005651]

I. INTRODUCTION

In a series of publications we have examined the electronic structure and bonding of the diatomic $3d$ -transition metal carbides MC=ScC,^{1(a)} TiC,^{1(b)} VC,^{1(c)} CrC,^{1(d)} MnC,^{1(e)} FeC,^{1(f),1(g)} CoC,^{1(h)} and NiC [Ref. 1(i)] through high level *ab initio* calculations. Albeit chemically “elementary,” these are computationally formidable systems whose definitive description is still a challenge to modern theoretical quantum chemistry. We also believe that the MCs are a terse system of molecules on which newly developed computational methodologies could be profitably tried and tested.

We presently report multireference configuration interaction (MRCI) and coupled-cluster (CC) calculations on the two lowest states of copper carbide, CuC, the last member of the MC sequence. To the best of our knowledge, there is a complete lack of experimental results on CuC, whereas theoretical investigations are limited to, in essence, a single density functional theory work.²

The following basis sets are used in the current work. For the Cu atom the cc-pV5Z (-NR and -DK) basis set,³ where -NR and -DK refer to nonrelativistic and Douglas-Kroll,⁴ respectively, and the cc-pwCV5Z (-NR and -DK) (Ref. 3) set for core-valence calculations, whereas for the C atom the cc-pV5Z (-NR and -DK) basis sets⁵ were employed.⁶ These were generally contracted to $[9s8p6d4f3g2h1i]_{Cu}+[6s5p4d3f2g1h]_C$ and $[11s10p8d5f4g3h2i]_{Cu}+[6s5p4d3f2g1h]_C$ for the valence and core-valence calculations, respectively.

The multireference methods selected are the active space self-consistent field+single+double replacements (CASSCF+1+2) and the averaged coupled pair functional (ACPF) (Ref. 7) within the internally contracted ansatz, as implemented in the MOLPRO 2006.1 suite of codes.⁸ The latter approach was employed to ameliorate the pernicious size nonextensivity errors introduced by the MRCI in a system of 15 valence electrons.

The single reference method used is the restricted CC singles+doubles+semi perturbative triples, RCCSD(T).⁹ At the RCCSD(T) level, we also performed core-valence calculations by including the intermediate core $3s^23p^6$ electrons of the Cu atom, tagged as C-RCCSD(T).

The orbital space used for both the single- and multireference correlation treatments was obtained from a state-averaged CASSCF wave function of the $4\Sigma^-$ and 2Π states using the $(2s+2p)$ valence space of C and the $4s$ orbital of Cu. The natural orbitals of the SA-CASSCF wave function were subsequently used for a full valence $(4s+3d+2s+2p)$ CI diagonalization of the Hamiltonian of either $4\Sigma^-$ or 2Π symmetry. The second set of natural orbitals was employed in the construction of the MRCI or ACPF wave functions as well as for the calculation of the RCCSD(T) energies. The same strategy was followed when scalar relativistic and core-valence correlation effects were taken into account.

The above computational scheme gives a coherent description of both $4\Sigma^-$ and 2Π states considering the severe problems encountered when one wishes to accurately describe the late $3d$ -transition metals.

An electronically congested $3d$ shell needs an additional set of diffuse d orbitals even at the most elementary quantum mechanical description as described in the literature from the late 1970s (Ref. 10) and these were added to the basis sets. It is nevertheless computationally impossible to extend the active space of the reference wave functions in order to account for the spatial inequivalence of the $3d$ electrons.

The inability to accurately describe the $3d^{10}$ and $3d^9$ atomic environments also extends to the study of the excited states of CuC. We were therefore forced to examine only the $4\Sigma^-$ and 2Π states which do not interact substantially with higher states of the same symmetry and which emanate from the excited states of both Cu and C.

For the two states studied, $4\Sigma^-$ and 2Π , we have constructed full potential energy curves (PECs) at the MRCI, ACPF, RCCSD(T) ($4\Sigma^-$) and MRCI and ACPF levels (2Π).

II. RESULTS AND DISCUSSION

The ground state configuration of the Cu atom is $3d^{10}4s^1(^2S)$ with the first excited state $3d^94s^2(^2D)$ located

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TABLE I. Total energies E (E_h), bond distances r_e (Å), dissociation energies D_e (kcal/mol), dipole moments μ_e (D), zero point energies ZPE (cm^{-1}), harmonic frequencies ω_e (cm^{-1}), and energy separations T_e (kcal/mol) of the $^4\Sigma^-$ and $^2\Pi$ states of $^{63}\text{Cu}^{12}\text{C}$ ($^{65}\text{Cu}^{12}\text{C}$).

Method ^a	$-E$	r_e	D_e	$\langle\mu_e\rangle/\mu_{\text{TF}}$ ^b	ZPE	ω_e	T_e
$^4\Sigma^-$							
MRCI	1677.260 70	1.848	41.0	4.5/4.9	281.1 (280.4)	559.1 (557.7)	0.0
MRCI+Q	1677.309 9	1.826	45.5	···/4.6	286.2 (285.5)	578.0 (576.6)	0.0
MRCI+DKH2	1691.440 77	1.813	42.4	4.3/4.6	295.0 (294.3)	585.9 (584.4)	0.0
MRCI+DKH2+Q	1691.491 2	1.792	47.1	···/4.3	303.4 (302.6)	607.5 (606.0)	0.0
ACPF	1677.313 44	1.818	50.6	3.9/4.2	286.6 (285.9)	574.7 (573.3)	0.0
ACPF+DKH2	1691.495 15	1.783	48.6	3.6/3.9	305.1 (304.3)	613.4 (611.8)	0.0
RCCSD(T)	1677.342 35	1.816	48.8	···/4.1	291.8 (291.1)	586.0 (584.6)	0.0
RCCSD(T)+DKH2	1691.52 478	1.783	50.5	···/3.9	308.2 (307.4)	620.2 (618.7)	1.5
C-RCCSD(T)	1677.827 98	1.819	48.1	···/4.1	290.4 (289.7)	580.6 (579.1)	0.0
C-RCCSD(T)+DKH2	1692.011 86	1.787	50.0	···/3.9	306.0 (305.3)	614.3 (612.7)	2.1
$^2\Pi$							
MRCI	1677.249 44	1.859	34.0	3.8/2.5	244.7 (244.1)	484.0 (482.9)	7.1
MRCI+Q	1677.301 8	1.827	40.5	···/2.4	266.6 (266.0)	532.6 (531.3)	5.1
MRCI+DKH2	1691.435 14	1.802	38.9	3.5/2.2	276.7 (276.0)	555.5 (554.2)	3.5
MRCI+DKH2+Q	1691.489 3	1.778	45.9	···/2.2	306.6 (305.8)	612.0 (610.5)	1.2
ACPF	1677.305 42	1.820	41.8	3.1/2.5	275.6 (275.0)	552.4 (551.0)	5.0
ACPF+DKH2	1691.493 24	1.773	47.4	2.8/2.3	315.0 (314.3)	635.7 (634.1)	1.2
RCCSD(T)	1677.338 06	1.808	46.2	···/2.6	299.6 (298.8)	601.0 (599.5)	2.7
RCCSD(T)+DKH2	1691.527 10	1.769	52.1	···/2.4	326.8 (326.0)	656.7 (655.1)	0.0
C-RCCSD(T)	1677.824 56	1.808	46.1	···/2.6	301.3 (300.6)	603.7 (602.2)	2.1
C-RCCSD(T)+DKH2	1692.015 16	1.772	51.9	···/2.4	328.2 (327.4)	656.0 (654.4)	0.0

^a+Q refers to the Davidson correction, DKH2 to the Douglas–Kroll–Hess second order scalar relativistic corrections, and C-RCCSD(T) takes into account core ($3s^23p^6$)-valence correlation.

^bDipole moments calculated as expectation values $\langle\mu_e\rangle$ and by the finite field approach, μ_{TF} . Field strengths of 10^{-5} – 10^{-4} a.u.

1.490 eV (M_J averaged) higher.¹¹ It is also of interest to mention the ratio of the expectation values of the $4s$ and $3d$ radii, $\langle r_{4s}\rangle/\langle r_{3d}\rangle \approx 3.4$ at the Hartree–Fock numerical level.¹² This means that the $3d^{10}$ electrons of Cu are well underneath the $4s^1$ distribution.

From the 2S state of Cu and the ground $^3P(2s^22p^2)$ state of C, four molecular states are derived, i.e., $^2,4\Sigma^-$ and $^2,4\Pi$. According to our calculations, the $^4\Sigma^-$ and $^2\Pi$ are relatively strongly bound, and the $^2\Sigma^-$ and $^4\Pi$ states weakly bound and of repulsive character, respectively. The valence-bond-Lewis (vbL) icons given below capture the bonding nature of the $^4\Sigma^-$ and $^2\Pi$ states.

The leading MRCI configuration functions and Mulliken atomic populations of the $^4\Sigma^-$ and $^2\Pi$ states completely reflect the vbL diagrams (valence electrons are counted only),

$$|^4\Sigma^-\rangle \approx 0.95|1\sigma^2 2\sigma^2 3\sigma^1 1\pi_x^2 1\pi_y^2 2\pi_x^1 2\pi_y^1 1\delta_+^1 1\delta_-^2\rangle$$

$$4s^{0.50} 4p_x^{0.04} 4p_y^{0.04} 4p_z^{0.08} 3d_{z^2}^{1.90} 3d_{xz}^{1.98} 3d_{yz}^{1.98} 3d_{x^2-y^2}^{1.98} 3d_{xy}^{1.99}/$$

$$2s^{1.72} 2p_z^{0.77} 2p_x^{0.97} 2p_y^{0.97}$$

and

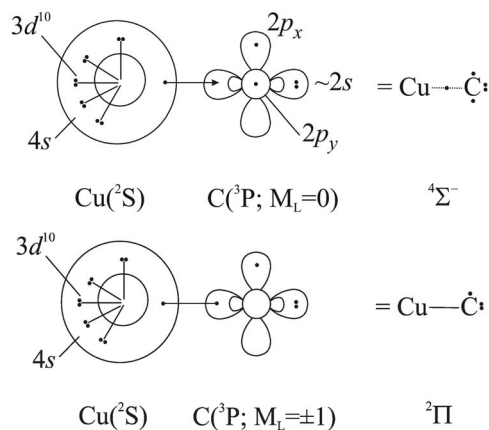
$$|^2\Pi\rangle \approx 0.92|1\sigma^2 2\sigma^2 3\sigma^2 1\pi_x^2 1\pi_y^2 2\pi_x^1 1\delta_+^1 1\delta_-^2\rangle$$

$$4s^{0.75} 4p_x^{0.04} 4p_y^{0.08} 3d_{z^2}^{1.90} 3d_{xz}^{1.97} 3d_{yz}^{1.91} 3d_{x^2-y^2}^{1.98} 3d_{xy}^{1.99}/$$

$$2s^{1.84} 2p_z^{1.34} 2p_x^{1.0} 2p_y^{0.12}.$$

Clearly in the $^4\Sigma^-$ state, the half sigma bond is formed by a

transfer of $0.5e^-$ from the $4s^1$ to the empty $2p_z$ orbital of the C atom, while in the $^2\Pi$ state the electron transfer in the σ -frame is limited to about $0.2e^-$ with an additional $0.1e^-$ along the π -frame. A small hybridization is also noticeable in both states between the $4s$ and $3d_{z^2}$ orbitals of the Cu atom.



From the diagrams given above, one would expect that the ground state ought to be of $^2\Pi$ symmetry due to the genuine $2-e^-$ sigma bond and a small $3d_{\pi}-2p_{\pi}$ delocalization, *vis-à-vis* a half (one electron) σ -bond of the $^4\Sigma^-$ state. However, the situation is more interesting as can be seen from Table I where pertinent numerical results are collected at MRCI (+Q), ACPF, and RCCSD(T) levels of theory. Fig-

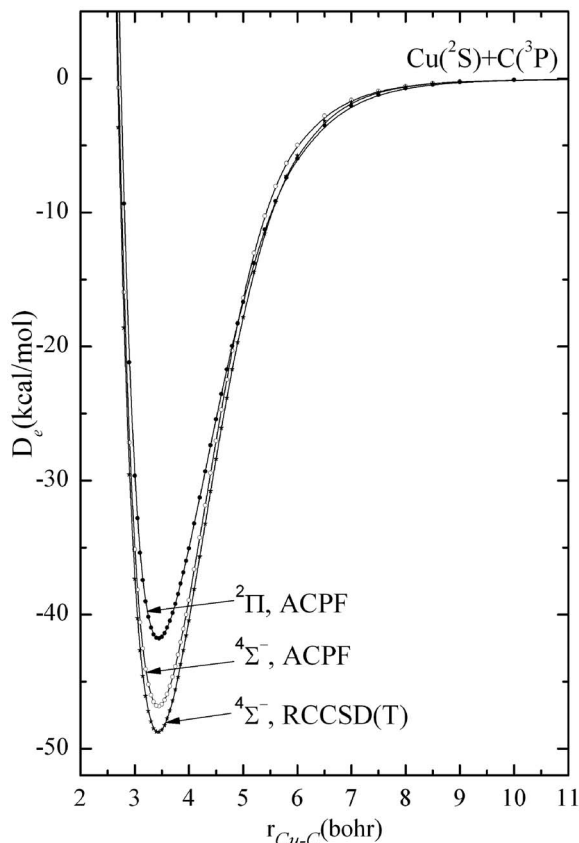


FIG. 1. ACPF ($^4\Sigma^-$ and $^2\Pi$) and RCCSD(T) ($^4\Sigma^-$) PECs of CuC; for the ordering of the states see text.

ure 1 displays PECs of the two studied states.

We observe that as we increase the level of theory from MRCI to MRCI+Q to ACPF to RCCSD(T) the $^4\Sigma^-$ - $^2\Pi$ separation decreases from 7.1 to 5.1 to 5.0 to 2.7 kcal/mol, respectively. Taking into account core-valence correlation effects [C-RCCSD(T)], T_e decreases further to 2.1 kcal/mol with the $^4\Sigma^-$ appearing consistently to be the ground state. Including relativity to the valence calculations through the DK Hamiltonian, the T_e diminishes by 3.6–3.9 (MRCI–MRCI+Q), 3.8 (ACPF), 2.7 [RCCSD(T)], and 2.1 [C–RCCSD(T)] kcal/mol. However, the combined effects of correlation and relativity at the RCCSD(T) or C-RCCSD(T) level makes finally $^2\Pi$ the ground state of CuC by 2.1 kcal/mol. It is fair to say though that within the accuracy of our calculations the two states are quasidegenerate with the $^2\Pi$ formally being the ground state.

Now, r_e and $D_e(D_0)$ values for both states converge monotonically with the level of calculation to 1.787 Å and 50.0 (49.1) kcal/mol for the $^4\Sigma^-$, with corresponding values of 1.772 Å and 51.9 (51.0) kcal/mol for the $^2\Pi$ state. As our numbers indicate, core-valence correlation effects are of minor importance for r_e and D_e alike, but relativistic effects influence significantly both r_e and D_e and for both states (see Table I). The same can be said concerning core-valence and relativistic effects for the dipole moment. Trusting more the finite-field values μ_{FF} ,¹³ our best dipole moment values converge to 3.9 D ($^4\Sigma^-$) and 2.4 D ($^2\Pi$). This large difference between the dipole moments is in harmony with the higher

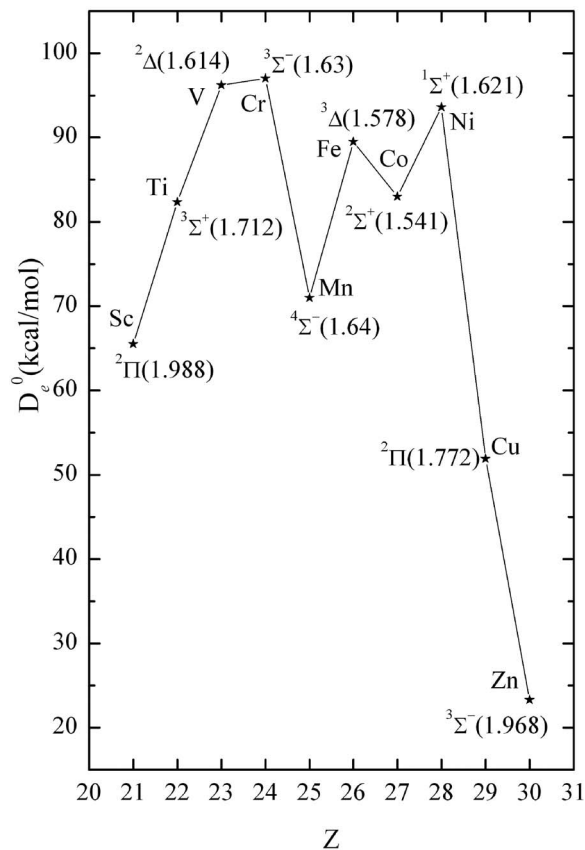


FIG. 2. Ground state symmetries and equilibrium bond distances (shown in parentheses and in Å) of all 3d-MCs in a $D_e^0(Z)$ diagram.

ionic character of the $^4\Sigma^-$ state according to the Mulliken charges, 0.48 ($^4\Sigma^-$) and 0.34 ($^2\Pi$) on the Cu atom.

It is interesting to contrast the CuC molecule with the simplest of “isovalent” species CH and CLi; the similarities are indeed remarkable. The ground state of CH is of $^2\Pi$ symmetry with the first excited state ($a^4\Sigma^-$) located 17.2 kcal/mol higher¹⁴ and with identical binding modes to the $^2\Pi$ and $^4\Sigma^-$ states of CuC. In CLi the order of these two states is reversed, i.e., $X^4\Sigma^-$ and $a^2\Pi$, with the latter about 30 kcal/mol higher¹⁵ and of the same binding nature to CH and CuC. In the CLi molecule there is a very substantial charge transfer from Li to C. Thus the ground state of the *in situ* C⁻ configuration is $2s^2 2p_x^1 2p_y^1 2p_z^1$ (4S projected to $^4\Sigma^-$), with the first excited state $2s^2 2p_x^1 2p_z^2$ (2D projected to $^2\Pi$) 1.229 eV (=28.3 kcal/mol) higher.^{16,17} This is the reason that in CLi the ground state is of $^4\Sigma^-$ symmetry. The opposite situation holds in the CH molecule where the bond is covalent and the ground state ($^2\Pi$) stems from the ground state atoms, whereas the $a^4\Sigma^-$ is formed from the 5S state of the C atom located 4.179 eV (Ref. 11) above the 3P state (see also Ref. 14). On the other hand, in CuC the bond is of “mixed character,” partly ionic and partly covalent, due to the higher ionization energy of Cu versus Li, namely, 7.726 and 5.392 eV,¹¹ respectively. Hence the quasidegeneracy of the $^2\Pi$ and $^4\Sigma^-$ states.

Concluding this report we would like to refer to Fig. 2 which positions the MC species in a $D_e^0 = D_e^0(Z)$ diagram, where $Z=21-30$ is the atomic number of M in the MC series.¹ The ZnC (Ref. 18) is also included for reasons of

completeness, although Zn can be hardly considered a 3d-transition metal element. Observe that in this \mathcal{M} -like diagram, CuC has the lowest binding energy of all MCs (MCs = Sc–Cu) and the longest bond length with the exception of ScC.

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