The electronic structure of the two lowest states of CuC

Apostolos Kalemos,1,a) Thom H. Dunning, Jr.,2,b) and Aristides Mavridis1,c)

1Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64 004, 157 10 Zografos Athens, Greece
2Department of Chemistry, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801, USA

(Received 5 August 2008; accepted 2 October 2008; published online 5 November 2008)

Theoretical and computational work on new forms of transition metal carbides, TiC, TiN, and Ti3C2, has appeared in the literature.10 The electronic structure of the two lowest states of CuC, 4Σ− and 3II, has been studied by a variety of methods. The combined effects of core-valence correlation and relativity point to an X-state of 3II symmetry with D = 51.9 kcal/mol and r = 1.772 Å. The 4Σ− state is predicted to lie 2.1 kcal/mol higher at r = 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 of the two lowest states of CuC, the last member of the transition metals. We have been particularly concerned with the nature of the bonding in these states and the extent to which relativistic effects should be included in any description of the electronic structure. The inability to accurately describe the 3II states has been attributed to the inability of existing ab initio methods to describe the relativistic effects.11,12

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-pVSZ (-NR and -DK) basis sets5 were employed.6 These were generally contracted to [9s8p6d4f3g2h1]Cu+[6s5p4d3f2g1h1]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.

II. RESULTS AND DISCUSSION

The ground state configuration of the Cu atom is 3d104s1(3S) with the first excited state 3d94s2(3D) located...
According to our calculations, the 4\Sigma^- and 2\Pi states of $^{63}$Cu $^{12}$C (65Cu $^{12}$C).

<table>
<thead>
<tr>
<th>Method $^a$</th>
<th>$-E$ (a.u.)</th>
<th>$r_e$ (Å)</th>
<th>$D_e$ (kcal/mol)</th>
<th>$(\mu_s/\mu_p)^b$</th>
<th>ZPE (cm$^{-1}$)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$T_e$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRCI</td>
<td>1677.260 70</td>
<td>1.848</td>
<td>41.0</td>
<td>4.5/4.9</td>
<td>281.1</td>
<td>559.1</td>
<td>557.7</td>
</tr>
<tr>
<td>MRCI+Q</td>
<td>1677.309 9</td>
<td>1.826</td>
<td>45.5</td>
<td>-4.6/4.6</td>
<td>286.2</td>
<td>578.0</td>
<td>576.6</td>
</tr>
<tr>
<td>MRCI+DKH2</td>
<td>1691.440 77</td>
<td>1.813</td>
<td>42.4</td>
<td>4.3/4.6</td>
<td>295.0</td>
<td>585.9</td>
<td>584.4</td>
</tr>
<tr>
<td>MRCI+DKH2+Q</td>
<td>1691.491 2</td>
<td>1.792</td>
<td>47.1</td>
<td>-4.3/4.3</td>
<td>303.4</td>
<td>607.5</td>
<td>606.0</td>
</tr>
<tr>
<td>ACPF</td>
<td>1677.313 44</td>
<td>1.818</td>
<td>50.6</td>
<td>3.9/4.2</td>
<td>286.6</td>
<td>574.7</td>
<td>573.3</td>
</tr>
<tr>
<td>ACPF+DKH2</td>
<td>1691.495 15</td>
<td>1.783</td>
<td>48.6</td>
<td>3.6/3.9</td>
<td>305.1</td>
<td>613.4</td>
<td>611.8</td>
</tr>
<tr>
<td>RCCSD(T)</td>
<td>1677.342 35</td>
<td>1.816</td>
<td>48.8</td>
<td>-4.1/4.1</td>
<td>291.8</td>
<td>586.0</td>
<td>584.6</td>
</tr>
<tr>
<td>RCCSD(T)+DKH2</td>
<td>1691.524 78</td>
<td>1.783</td>
<td>50.5</td>
<td>-3.9/3.9</td>
<td>308.2</td>
<td>620.2</td>
<td>618.7</td>
</tr>
<tr>
<td>C-RCCSD(T)</td>
<td>1677.827 98</td>
<td>1.819</td>
<td>48.1</td>
<td>-4.1/4.1</td>
<td>290.4</td>
<td>580.6</td>
<td>579.1</td>
</tr>
<tr>
<td>C-RCCSD(T)+DKH2</td>
<td>1692.011 86</td>
<td>1.787</td>
<td>50.0</td>
<td>-3.9/3.9</td>
<td>306.0</td>
<td>614.3</td>
<td>612.7</td>
</tr>
</tbody>
</table>

$^4$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$^2$3p$^6$)-valence correlation.

$^b$ Dipole moments calculated as expectation values $\langle \mu_s \rangle$ and by the finite field approach, $\mu_{ff}$. Field strengths of 10$^{-3}$–10$^{-4}$ a.u.

1.490 eV (Mf averaged) higher. 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. This means that the 3d$^{10}$ electrons of Cu are well underneath the 4s$^1$ distribution.

From the $^3$S state of Cu and the ground $^3P(2s^22p^2)$ state of C, four molecular states are derived, i.e. $^4\Sigma^-$ and $^2\Pi$. According to our calculations, the $^4\Sigma^-$ and $^2\Pi$ are relatively strongly bound, and the $^2\Sigma^-$ and $^2\Pi$ 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),

\[
\begin{align*}
| ^4\Sigma^- \rangle &= 0.95 | 1s^22s^22p^63s^23p^63d^14s^1 \rangle + 0.05 | 1s^22s^22p^63s^23p^63d^14s^1 \rangle \\
&= 4s_{0.50}p_x^{0.44}p_y^{0.44}p_z^{0.08}d_{x^2}^{0.93}d_{y^2}^{0.98}d_{z^2}^{0.98}d_{xy}^{3.59}/2s_{1.72}^{2.77}p_x^{0.97}p_y^{0.97},
\end{align*}
\]

and

\[
\begin{align*}
| ^2\Pi \rangle &= 0.92 | 1s^22s^22p^63s^23p^63d^14s^1 \rangle + 0.08 | 1s^22s^22p^63s^23p^63d^14s^1 \rangle \\
&= 4s_{0.74}p_x^{0.44}p_y^{0.08}d_{x^2}^{0.90}d_{y^2}^{3.97}d_{z^2}^{3.91}d_{xy}^{3.98}d_{x^2-y^2}^{3.98}d_{xy}^{3.98}/2s_{1.84}^{1.84}p_x^{1.02}p_y^{1.02},
\end{align*}
\]

Clearly, in the $^2\Sigma^-$ 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 $\sigma$-frame is limited to about 0.2e$^-$ with an additional 0.1e$^-$ along the $\pi$-frame. A small hybridization is also noticeable in both states between the 4s and 3d$_{x^2}$, 3d$_{y^2}$, and 3d$_{z^2}$ orbitals of the Cu atom.

![Diagram of the Cu-C bond](Image)

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 $3d_{x^2}$-$2p_{\pi}$ delocalization, via $\pi$-$\pi$-vis a half (one electron) $\sigma$-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-

Downloaded 06 Nov 2008 to 195.134.76.131. Redistribution subject to ASCE license or copyright; see http://jcp.aip.org/jcp/copyright.jsp
The structure of the two lowest states of CuC


The ordering of the states see text.

FIG. 1. ACPF (4Σ− and 2Π) and RCCSD(T) (4Σ−) PECs of CuC; for the ordering of the states see text.

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

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 4Σ−-2Π separation decreases from 7.1 to 5.1 to 5.0 to 2.7 kcal/mol, respectively. Taking into account core-valence correlation effects decreases from 7.1 to 5.1 to 5.0 to 2.7 kcal/mol, monotonically with the level of calculation to 1.787 Å and 49.1 kcal/mol higher than the ground state of CuC by 2.1 kcal/mol. However, the combined effects of correlation and relativity at the RCCSD level makes finally the ground state of CuC by 2.1 kcal/mol.

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 4Σ−, with corresponding values of 1.772 Å and 51.9 (51.0) kcal/mol for the 2Π 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 1). The same can be said concerning core-valence and relativistic effects for the dipole moment. Trusting more the finite-field values μ_FF, our best dipole moment values converge to 3.9 D (4Σ−) and 2.4 D (2Π). This large difference between the dipole moments is in harmony with the higher ionic character of the 4Σ− state according to the Mulliken charges, 0.48 (4Σ−) and 0.34 (2Π) 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 2Π symmetry with the first excited state (a 4Σ−) located 17.2 kcal/mol higher and with identical binding modes to the 2Π and 4Σ− states of CuC. In CLi the order of these two states is reversed, i.e., X 4Σ− and a 2Π, with the latter about 30 kcal/mol higher 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^22p^22p^1(4Σ−) projected to 4Σ−, with the first excited state 2s^22p^12p^1(4Π) projected to 2Π) 1.229 eV (≈28.3 kcal/mol) higher. This is the reason that in CLi the ground state is of 4Σ− symmetry. The opposite situation holds in the CH molecule where the bond is covalent and the ground state (2Π) stems from the ground state atoms, whereas the a 4Σ− is formed from the 1Σ 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, respectively. Hence the quasidegeneracy of the 2Π and 4Σ− states.

Concluding this report we would like to refer to Fig. 2 which positions the MC species in a D^0(Z) diagram, where Z=21–30 is the atomic number of M in the MC series. 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 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.