On the ground electronic states of copper silicide and its ions

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(Received 3 April 1997; accepted 7 January 1998)

The low-lying electronic states of SiCu, SiCu+, and SiCu− have been studied using a variety of high-level ab initio techniques. As expected on the basis of simple orbital occupancy and bond forming for Si(s2p2)+Cu(s1) species, 1Πg, 1Σg+, and 3Σg− states were found to be the ground electronic states for SiCu, SiCu+, and SiCu−, respectively; the 2Πu state is not that suggested in most recent experimental studies. All of these molecules were found to be quite strongly bound although the bond lengths, bond energies, and harmonic frequencies vary slightly among them, as a result of the nonbonding character of the 2π-MO (molecular orbital) [composed almost entirely of the Si 3p-AO (atomic orbital)], the occupation of which varies from 0 to 2 within the 1Σg+, 2Πu, and 3Σg− series. The neutral SiCu is found to have bound excited electronic states of 4Σg−, 2Δg, 2Σg+, and 2Πu symmetry lying 0.5, 1.2, 1.8, and 3.2 eV above the 2Πu ground state. It is possible but not yet certain that the 2Πu state is, in fact, the “B state” observed in the recent experimental studies by Scherer, Paul, Collier, and Saykally. © 1998 American Institute of Physics.

I. INTRODUCTION

In recent cavity ringdown laser absorption spectroscopy (CRLAS) studies of Scherer et al.,1 the first copper silicide spectra were measured in the UV-vis region from 410 to 380 nm. The observed UV (ultraviolet) band system (labeled as B-X) consisted of a single vibronic progression in the upper electronic state. The B label for the upper state was chosen based on the likelihood that the band origin was too high in energy to correspond to the first excited state, combined with the fact that additional unassigned spectra were measured to the red only under conditions which favored CuSi production. In that initial work, rotational resolution was achieved, yet no Q-branches were observed. A 2Σ state assignment was thus given for both the upper and lower states observed from several factors, although the likelihood of a 2Π ground state is strongly indicated based on simple orbital occupancy considerations. A primary focus of the present work has been to sort out this confusion surrounding the 2Π and 2Σ state orderings.

Specifically, a basic description of the ground-state bonding in CuSi involves combining ground-state Cu atom (3d10 4s1) with the 3s2 3p2 configuration of Si. In the L-S coupling limit, this amounts to finding the states resulting from combining a 2S Cu atom with the 3P, 1D, and 1S states of the Si atom. States resulting from the combination of the lowest 2S and 3P terms are of 2Σ−, 2Π, 4Σ−, and 4Π symmetry, while states resulting from the 2S and 1D combination would possess 2Σ+, 2Π, and 2Δ symmetry. Finally, the addition of 2S and 1S asymptotes produces only a 2Σ+ state.

Since the ground state of Si is 3P, one would predict the ground state of SiCu to be of 2Π symmetry, derived from pairing the Cu s-electron with a pγ electron of Si while retaining one pγ electron. However, in the event that bond-
tion theory (MP2),\textsuperscript{10} and quadratic configuration interaction methods including all single- and double-excitation (QCISD).\textsuperscript{11} The energies of the lowest electronic states were then refined at the higher QCISD(T)/6-311++G(2d,2p) level using the QCISD/6-311++G(d,f) optimized geometries. Only the findings at the QCISD and QCISD(T) levels are reported since they are our best predictions. The unrestricted MP2 (UMP2) wave functions for open-shell systems were spin-projected to produce purer spectroscopic states (PMP2).\textsuperscript{12} All calculations were carried out with the GAUSSIAN 94\textsuperscript{13} suite of programs and core orbitals were (Si 1s-2p and Cu 1s-3p) were frozen in all correlated calculations; the Cu \textit{d} electrons were included, not frozen.

Because some states (e.g., the Σ\textsuperscript{+} and Π\textsuperscript{2}) cannot be properly described by a single determinant, the geometries and harmonic vibrational frequencies of SiCu were also studied using the complete active space self-consistent field—multireference configuration interaction method, including all single and double excitations from the reference configurations (CASSCF-MRCISD)\textsuperscript{14,15} using the ANO basis set of Pierloot \textit{et al.}\textsuperscript{16} within the MOLCAS-3 program.\textsuperscript{17}

The CASSCF/MRCISD energies were corrected by the Davidson method\textsuperscript{18,19} [CASSCF/MRCISD(Q)] to account for the quadruple and higher order excited configurations. Finally, the Vibrot program from the MOLCAS-3 package was used for numerically solving the one-dimensional Schrödinger equation to obtain the molecular vibrational parameters at this CASSCF-MRCISD(Q) level. Due to the computational demands of this approach, the Cu 3\textit{d} electrons could not be included in the correlation energy calculations. As a result, the CASSCF/MRCISD data are not as accurate as the QCISD and QCISD(T) predictions, but are essential for states with more than one dominant determinant.

### III. Results and Discussions

The results of our calculations for SiCu, SiCu\textsuperscript{+}, and SiCu\textsuperscript{2+} are presented in Table I. The dissociation energies for SiCu, SiCu\textsuperscript{+}, and SiCu\textsuperscript{2+} and the ionization potential and electron affinity for SiCu are summarized in Table II.

<table>
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<tr>
<th></th>
<th>SiCu\textsuperscript{(+)}</th>
<th>SiCu\textsuperscript{(+\textsuperscript{2})}</th>
<th>SiCu\textsuperscript{(+\textsuperscript{2}\textsuperscript{2})}</th>
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<tr>
<td>(1\sigma\textsuperscript{2}1\delta\textsuperscript{1}1\pi\textsuperscript{2}\textsuperscript{1}\pi\textsuperscript{2}\textsuperscript{2}\pi)</td>
<td>QCISD/6-311++G(d,f)</td>
<td>QCISD/6-311++G(d,f)</td>
<td>QCISD/6-311++G(d,f)</td>
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<tr>
<td>(E_{\text{QCISD}})</td>
<td>-1928.172 526</td>
<td>-1928.156 300</td>
<td>-1928.041 555</td>
</tr>
<tr>
<td>(R_{\text{s}}\text{(Si-Cu)})</td>
<td>2.242 Å</td>
<td>2.226 Å</td>
<td>2.176 Å</td>
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<tr>
<td>(\omega_{\text{s}})</td>
<td>336 cm\textsuperscript{-1}</td>
<td>320 cm\textsuperscript{-1}</td>
<td></td>
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<tr>
<td>(\langle S^2 \rangle)</td>
<td>0.760</td>
<td>3.761</td>
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<tr>
<td>(T_{\text{e}}\text{QCISD})</td>
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<td>0.442 eV</td>
<td>3.564 eV</td>
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<tr>
<td>(Q_{\text{NPA}(Si)})</td>
<td>-0.073 e</td>
<td>-0.495 e</td>
<td>-0.738 e</td>
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<td>(\mu_e)</td>
<td>1.396 D</td>
<td>3.253 D</td>
<td>3.381 D</td>
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<tr>
<td>QCISD(T)/6-311++G(2d,2p)</td>
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<td></td>
<td></td>
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<tr>
<td>(E_{\text{QCISD(T)}})</td>
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<td>(Q_{\text{NPA}(Si)})</td>
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<td>0.501 eV</td>
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<td>(\mu_e)</td>
<td>1.139 eV</td>
<td>0.054 e</td>
<td>2.107 e</td>
</tr>
</tbody>
</table>

*Optimized at QCISD/6-311++G(d,f).*
A. SiCu

We studied what are probably the three lowest electronic states: \( ^2 \Pi_i (1 \sigma^2 1 \delta^2 2 \pi^2 3 \sigma^2 2 \pi^4) \), \( ^4 \Sigma^- (1 \sigma^2 1 \delta^1 1 \pi^1 2 \sigma^2 3 \sigma^1 2 \pi^2) \), \( ^4 \Pi_i (1 \sigma^2 1 \delta^1 1 \pi^1 2 \sigma^2 3 \sigma^2 2 \pi^4) \), and \( ^4 \Pi_i (1 \sigma^2 1 \delta^1 1 \pi^2 2 \sigma^3 3 \sigma^1 2 \pi^2) \) at the CASSCF, MP2, and QCISD levels of theory. The \( ^2 \Delta \sigma^2 1 \delta^1 1 \pi^2 2 \sigma^2 3 \sigma^2 2 \pi^2 \) and \( ^2 \Sigma^- [1 \sigma^2 1 \delta^1 1 \pi^1 2 \sigma^2 3 \sigma^1 2 \pi^2 + 2 \pi^4] \) states were examined at the CASSCF/MRCISD level of theory because of their intrinsically multideterminantal nature. Notice that we number only the valence orbitals as a result of which the Cu–Si σ-bond is the 2σ orbital. The states considered involve double occupancy of the 3d orbitals of Cu, as well as for the bonding 2σ-MO with the three other valence electrons distributed throughout the 3σ, 4σ, and 2π valence orbitals.

The \( ^2 \Pi_i \) state was found to be the ground state at all three (B3LYP, MP2, and QCISD) levels of theory, and all three methods give very similar bond lengths (2.24 Å), harmonic frequencies (~336 cm\(^{-1}\)) and dissociation energies (~1.8 eV). In this state, we find the unpaired spin density to be located completely on the silicon atom, we find it to be very ionic (\( \mu_s = 1.4 \) D) and the calculated harmonic frequency and dissociation energy both suggest strong bonding in this ground state of SiCu. At the CASSCF/MRCISD and CASSCF/MRCISD(Q) levels of theory, the calculated bond lengths are longer: 2.44 and 2.52 Å and the frequencies are softer: 249 and 235 cm\(^{-1}\), respectively, than for our most accurate data at the QCISD level of theory. This is a result of neglecting the Cu 3d electrons in the CASSCF/MRCISD correlation calculations, not because of any multiconfigurational nature of this state for which the Hartree–Fock (HF) configuration is dominate (\( C_{HF} = 0.93 \)).

A \( ^4 \Sigma^- \) state arising from promoting one electron from the nonbonding 3σ-MO into the 2π-MO is the lowest excited state with a 0.47 eV excitation energy the QCISD(T)/6-311++G(2d,2p) level of theory. This state is more ionic (\( \mu_s = 3.3 \) D) than the ground state and has most (i.e., 2.4 e) of the unpaired electron density located mostly on the silicon atom. Both the ground and this first excited states are strongly bound with very similar bond lengths and harmonic frequencies.

A bound \( ^2 \Pi_i \) doublet state arising from promotion of two electrons from the 3σ-MO into the 2π-MO is substantially higher (~3.2 eV at QCISD(T)/6-311++G(2d,2p)) in energy, is even more ionic (\( \mu_s = 3.4 \) D) and does lie in the region where Scherer et al. observed a \( \Delta L(\Omega) = 0 \) transition. It is possible that the \( ^2 \Pi_i \) state is, in fact, the ‘‘B state’’ observed in that study, since the ground state \( ^2 \Pi_i \) has the same symmetry. To more carefully examine this possibility we performed CASSCF/MRCISD calculations for the second and third roots of \( ^2 \Pi_i \) symmetry (the \( ^2 \Pi_i \) ground state being the first root). The second root was found to be very multiconfigurational, to have the dominant \( (2 \sigma^2 3 \sigma^2 4 \sigma^2 2 \pi^2) = 0.72 \) configuration in the MRCISD expansion, and to be repulsive at CASSCF/MRCISD level of theory. The third root is also quite multiconfigurational with the dominant \( (2 \sigma^2 3 \sigma^2 4 \sigma^2 2 \pi^2) = 0.63 \) configuration in the MRCISD expansion, and has a minimum at \( r_s = 2.41 \) Å with the harmonic frequency of 209 cm\(^{-1}\). As for the \( ^2 \Pi_i \) ground state, we expect that this bond length is too long because Cu 3d electron correlation is neglected. However, the excitation energy from the \( ^2 \Pi_i \) ground state to this state 3.17 eV is close to the 3.22 eV obtained at the QCISD(T) level of theory and to the experimentally observed transition.

As stated earlier, we needed to use the multiconfigurational based CASSCF (4a\(_1\), 2b\(_1\), 2b\(_2\), 1a\(_1\) active space within \( C_{\sigma}\) symmetry) method to treat the \( ^2 \Sigma^+ \) and \( ^2 \Delta \) states. After so doing and using the CASSCF/MRCISD(Q) energy for the \( ^2 \Pi_i \) ground state, we find the \( ^2 \Delta \) and \( ^2 \Sigma^+ \) states (obtained as the lowest roots among the doublet states within \( a_1\)-symmetry) to have excitation energies of 1.21 and 1.76 eV, respectively, above the ground \( ^2 \Pi_i \) state.

In summary, for SiCu we found the following state ordering:

- \( ^2 \Pi_i \rightarrow ^4 \Sigma^- \) 0.5 eV
- \( ^2 \Pi_i \rightarrow ^2 \Delta \) 1.2 eV
- \( ^2 \Pi_i \rightarrow ^2 \Sigma^+ \) 1.8 eV
- \( ^2 \Pi_i \rightarrow ^2 \Pi_i \) 3.2 eV

B. SiCu\(^+\)

We studied three low-lying cation electronic states: \( ^1 \Sigma^+ (1 \sigma^2 1 \delta^1 1 \pi^1 2 \sigma^2 3 \sigma^2 2 \pi^2) \), \( ^3 \Pi_i (1 \sigma^2 1 \delta^1 1 \pi^2 2 \sigma^2 3 \sigma^2 2 \pi^4) \), and \( ^3 \Sigma^- (1 \sigma^2 1 \delta^1 1 \pi^1 2 \sigma^2 3 \sigma^5 2 \pi^2) \) all of which involve double occupancy for the 3d orbitals of Cu and of the bonding 2σ-MO with the two remaining valence electrons distributed throughout the 3σ and 2π valence orbitals. The \( ^1 \Sigma^+ \) state was found to be the ground state at all three (B3LYP, MP2, and QCISD) levels of theory; again all three methods give very similar bond lengths, harmonic frequencies, and dissociation energies.

The calculated adiabatic ionization energy of SiCu was found to be 7.01 eV at our highest QCISD(T)/6-311++G(2d,2p) level of theory (see Table II). The harmonic frequency (358 cm\(^{-1}\)) and dissociation energy (\( D_e = 2.16 \) eV) obtained for the ground state of SiCu\(^+\), both suggest strong bonding (both are somewhat larger than the corresponding values for the neutral molecule).

The \( ^3 \Pi_i \) cation state arising from promoting of one electron from the 3σ-MO into the 2π-MO was found to be 0.50 eV above the ground electronic state. A \( ^3 \Sigma^- \) state was found to be substantially higher in energy, so the \( ^3 \Sigma^- \) state is reasonably well established to be the ground electronic state of SiCu\(^+\).
C. SiCu$^-$

We studied six low-lying anion electronic states $^3\Sigma^-(1s^2\delta^11\pi^42\sigma^23\sigma^22\pi^2)$, $^3\Pi_1(1s^2\delta^1\pi^42\sigma^23\sigma^22\pi^23\pi^3)$, $^3\Sigma^+(1s^2\delta^1\pi^42\sigma^23\sigma^22\pi^24\sigma^2)$, $^1\Pi_1(1s^2\delta^1\pi^42\sigma^23\sigma^22\pi^24\sigma^23\pi^4)$, and $^1\Sigma^+(1s^2\delta^1\pi^42\sigma^23\sigma^22\pi^24\sigma^24\pi^4)$ derived using double occupancy for the 3d orbitals of Cu as well as for the bonding 2p-MO with the four other valence electrons distributed throughout the 3s, 4s, and 2p valence orbitals. The $^1\Sigma^+$ (1s$^2$\delta$^1$1\pi$^2$2\sigma$^2$3\sigma$^2$2\pi$^2$) state was not considered here, because we assume that the higher multiplicity $^3\Sigma^-$ state with the same orbital occupancy will be lower in energy.

The $^3\Sigma^-$ state was found to be the ground state at all three (B3LYP, MP2, and QCISD) levels of theory, and again all three methods give very similar bond lengths, harmonic frequencies, and dissociation energies. The calculated adiabatic electron affinity of SiCu was found to be 1.42 eV at our highest QCISD(T)/6-311+ +G(2d,2p) level of theory (see Table II). Our calculated harmonic frequency ($283 \text{ cm}^{-1}$) and dissociation energy into the lowest energy asymptote Si$^-$($^4S$)+Cu($^2S$) ($D_e=2.04 \text{ ev}$) both suggest strong bonding in the ground state of SiCu$^-$. $^5\Sigma^-$ and $^3\Pi_1$ states arising from promoting one electron from the 3σ-MO into the 4σ-MO and promoting one electron from the 2σ-MO into the 4σ-MO, respectively, are the lowest excited state with 1.09 and 1.14 eV excitation energies. Three other states $^3\Sigma^+$, $^1\Sigma^+$, and $^1\Pi_1$ are substantially higher in energy, so the $^3\Sigma^-$ state is well established to be the ground electronic state for SiCu$^-$. 

IV. SUMMARY

In summary, we found that the Aufbau principle correctly predicts the ground electronic states for SiCu, SiCu$^+$, and SiCu$^-$, all of which were found to be relatively strongly bound although the bond lengths, bond energies, and harmonic frequencies vary slightly among these species. These small variations are a result of the nonbonding character of the 2σ-MO, which is almost completely composed of the Si 3p-AO. Of special relevance to the CRLAS study of Scherer et al.$^1$ is the fact that SiCu is likely to have a $^2\Pi_1$ ground state, not the $^2\Sigma^+$ state suggested earlier. In light of these findings, the analogous CRLAS studies of Scherer et al.$^{20,21}$ on the similar SiAg and SiAu molecules will also need to be reexamined.

In this work, we used sophisticated $ab\ initio$ methods to calculate molecular properties of the ground and lowest excited electronic states of SiCu, SiCu$^+$, and SiCu$^-$. Our results are very similar at the density functional theory (B3LYP), second-order Möller–Plesset perturbation theory (MP2) and quadratic configuration level (QCISD), when valence-triple-zeta bases sets augmented by sets of diffuse s- and p-functions and sets of polarization functions have been used. In all of these calculations, all core electrons were excluded from correlation but the 3d-electrons of Cu were included. Recently we studied the isoelectronic AlZn diatomic molecule at the QCISD/6-311+ +G* and QCISD(T)/6-311+ +G* levels of theory and found that triple excitations are very important for proper description of the vibrational frequency.$^{22}$ We therefore reexamined the geometries and frequencies of SiCu, SiCu$^+$, and SiCu$^-\text{ at QCISD(T)/6-311+ +G* level of theory.}$ The calculated molecular parameters at this level of theory: $r_e=2.235 \text{ Å}$ and $\omega_e=325 \text{ cm}^{-1}$ for SiCu ($^2\Pi_1$); $r_e=2.258 \text{ Å}$ and $\omega_e=311 \text{ cm}^{-1}$ for SiCu$^+$ ($^1\Sigma^+$) and $r_e=2.268 \text{ Å}$ and $\omega_e=270 \text{ cm}^{-1}$ for SiCu$^-$ ($^3\Sigma^-$) are very close to those found at the QCISD/6-31+ +G* level of theory. Therefore for the species studied here triple excitations were found not to be important.

Finally, we would like to stress that while diatomic molecules are the simplest chemical species, most have not yet been fully characterized either theoretically or experimentally. Recently two of us (A.I.B. and J.S.) created three diatomic periodic tables (main group dimers, transition metal dimers, and mixed dimers),$^{23}$ which summarize all that is known about the term symbols, bond lengths, and dissociation energies of diatomic species. In these tables there are many species for which nothing or little is known. Taking into account the importance of high quality data on diatomic molecules for understanding chemical bonding among atoms in larger molecules, we hope that more efforts will be made to fill in the missing data in these Tables.

ACKNOWLEDGMENTS

The authors wish to thank Professor Michael Morse and Professor Richard Barrow for bringing to their attention the possibility that SiCu might have a $^2\Pi$ rather than $^2\Sigma$ ground electronic state. This theoretical work was supported by NSF Grant No. CHE9116286. The Saykally CRLAS studies were supported by the AFORS Grant No. F49620-96-1-0411.

17. MOLCAS Version 3, K. Andersson, M. R. A. Blomberg, M. P. Fulscher, V.


