On the ground electronic states of copper silicide and its ions

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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(s^2p^2)+Cu(s^1) species, $^2\Pi_r$, $^1\Sigma^+$, and $^3\Sigma^-$ states were found to be the ground electronic states for SiCu, SiCu$^+$, and SiCu$^-$, respectively; the $^2\Pi_r$ 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 $^1\Sigma^+$, $^2\Pi_r$, and $^3\Sigma^-$ series. The neutral SiCu is found to have bound excited electronic states of $^4\Sigma^-$, $^2\Delta$, $^2\Sigma^+$, and $^2\Pi_i$ symmetry lying 0.5, 1.2, 1.8, and 3.2 eV above the $^2\Pi_r$ ground state. It is possible but not yet certain that the $^2\Pi_i$ state is, in fact, the ''B state'' observed in the recent experimental studies by Scherer, Paul, Collier, and Saykally. © *1998 American Institute of Physics.*
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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 $^2\Sigma$ state assignment was thus given for both the upper and lower states observed from several factors, although the likelihood of a $^2\Pi$ 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 $^2\Pi$ and $^2\Sigma$ state orderings.

Specifically, a basic description of the ground-state bonding in CuSi involves combining ground-state Cu atom ($3d^{10}4s^1$) with the $3s^23p^2$ 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 $^2\Sigma^-$, $^2\Pi$, $^4\Sigma^-$, and $^4\Pi$ symmetry, while states resulting from the ^2S and ^1D combination would possess $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ symmetry. Finally, the addition of ^2S and ^1S asymptotes produces only a $^2\Sigma^+$ state.

Since the ground state of Si is ^3P, one would predict the ground state of SiCu to be of $^2\Pi$ symmetry, derived from pairing the Cu *s*-electron with a p_σ electron of Si while retaining one p_π electron. However, in the event that bond-ing arises from excited Si asymptotes, a $^2\Sigma^+$ state would be more likely. The CRLAS data[1] obtained were consistent with either of these possibilities. However, spectral congestion in the origin region precluded definitive assignment. Due to the lack of observed *Q*-branches, it was only possible to rigor-ously assign these bands as belonging to $\Delta L(\Omega)=0$ (i.e., $\Sigma\rightarrow\Sigma$ or $\Pi\rightarrow\Pi$) transitions. In the event of the $L>0\rightarrow L>0$ assignment, one would expect a very weak *Q*-branch, which would rapidly decrease in transition strength with in-creasing *J*. Given the 50 K rotational temperatures typically achieved in the silane-seeded laser ablation beams, *Q*-branches of this type could have easily been obscured by other *P* and *R*-branch lines from the three most abundant CuSi isotopes. For these reasons, Scherer *et al.*[1] adopted the $^2\Sigma$ lower state assignment, again recognizing the possibility that the observed bands could instead be due to $\Pi\rightarrow\Pi$ tran-sitions, wherein the expected weak *Q*-branches might not be resolved. Finally, it is possible that the transitions observed actually originate from an excited CuSi state, and do not, in fact, originate from the ground state.

II. COMPUTATIONAL DETAILS

The bond lengths and harmonic vibrational frequencies of the lowest electronic states of SiCu, SiCu$^+$, and SiCu$^-$ were optimized using analytical gradients and polarized split-valence basis sets of 6-311++G(d,f) quality[2–7] [++ denotes diffuse s,p-functions on Si and diffuse d-functions on Cu and (d,f) denotes polarization d-functions on Si and polarization f-functions on Cu] within the density functional theory (B3LYP),[8,9] second-order Møller–Plesset perturba-

TABLE I. Calculated molecular properties of the lowest bound SiCu, SiCu$^+$, and SiCu-States.

SiCu($^2\Pi_r$)	SiCu($^4\Sigma^-$)	SiCu($^2\Pi_i$)
$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1$	$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2$	$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^3$
QCISD/6-311++G(d,f)	QCISD/6-311++G(d,f)	QCISD/6-311++G(d,f)
$E_{\text{QCISD}}= -1928.172\,526$	$E_{\text{QCISD}}= -1928.156\,300$	$E_{\text{QCISD}}= -1928.041\,555$
R_e(Si–Cu)= 2.242 Å	R_e(Si–Cu)= 2.226 Å	R_e(Si–Cu)= 2.176 Å
ω_e= 336 cm^{-1}	ω_e= 320 cm^{-1}	
$\langle S^2 \rangle$= 0.760	$\langle S^2 \rangle$= 3.761	$\langle S^2 \rangle$= 0.869
$T_{e,\text{QCISD}}$= 0.0 eV	$T_{e,\text{QCISD}}$= 0.442 eV	$T_{e,\text{QCISD}}$= 3.564 eV
Q^{NPA}(Si)= −0.073 e	Q^{NPA}(Si)= −0.495 e	Q^{NPA}(Si)= −0.738 e
μ_e= 1.396 D	μ_e= 3.253 D	μ_e= 3.381 D
QCISD(T)/6-311++G($2d,2f$)	QCISD(T)/6-311++G($2d,2f$)	QCISD(T)/6-311++G($2d,2f$)
$E_{\text{QCISD(T)}}= -1928.255\,029^{\text{a}}$	$E_{\text{QCISD(T)}}= -1928.237\,914^{\text{a}}$	$E_{\text{QCISD(T)}}= -1928.136\,847^{\text{a}}$
$T_{e,\text{QCISD(T)}}$= 0.0 eV	$T_{e,\text{QCISD(T)}}$= 0.466 eV	$T_{e,\text{QCISD(T)}}$= 3.216 eV
SiCu$^+$($^1\Sigma^+$)	SiCu$^+$($^3\Pi_r$)	SiCu$^+$($^3\Sigma^-$)
$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0$	$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1$	$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^2$
QCISD/6-311++G(d,f)	QCISD/6-311++G(d,f)	QCISD/6-311++G(d,f)
$E_{\text{QCISD}}= -1927.924\,676$	$E_{\text{QCISD}}= -1927.904\,267$	$E_{\text{QCISD}}= -1927.848\,560$
R_e(Si–Cu)= 2.257 Å	R_e(Si–Cu)= 2.357 Å	R_e(Si–Cu)= 2.407 Å
ω_e= 358 cm^{-1}	ω_e= 240 cm^{-1}	ω_e= 179 cm^{-1}
	$\langle S^2 \rangle$= 2.014	$\langle S^2 \rangle$= 2.107
$T_{e,\text{QCISD}}$= 0.0 eV	$T_{e,\text{QCISD}}$= 0.555 eV	$T_{e,\text{QCISD}}$= 2.071 eV
Q^{NPA}(Si)= +0.633 e	Q^{NPA}(Si)= +0.297 e	Q^{NPA}(Si)= +0.054 e
QCISD(T)/6-311++G($2d,2f$)	QCISD(T)/6-311++G($2d,2f$)	QCISD(T)/6-311++G($2d,2f$)
$E_{\text{QCISD(T)}}= -1927.997\,449^{\text{a}}$	$E_{\text{QCISD(T)}}= -1927.979\,082^{\text{a}}$	$E_{\text{QCISD(T)}}= -1927.924\,404^{\text{a}}$
$T_{e,\text{QCISD(T)}}$= 0.0 eV	$T_{e,\text{QCISD(T)}}$= 0.501 eV	$T_{e,\text{QCISD(T)}}$= 1.988 eV
SiCu$^-$($^3\Sigma^-$)	SiCu$^-$($^5\Sigma^-$)	SiCu$^-$($^3\Pi_r$)
$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2$	$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^1$	$1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^1$
QCISD/6-311++G(d,f)	QCISD/6-311++G(d,f)	QCISD/6-311++G(d,f)
$E_{\text{QCISD}}= -1928.217\,470$	$E_{\text{QCISD}}= -1928.182\,600\,7$	$E_{\text{QCISD}}= -1928.187\,167$
R_e(Si–Cu)= 2.262 Å	R_e(Si–Cu)= 2.330 Å	R_e(Si–Cu)= 2.278 Å
ω_e= 283 cm^{-1}	ω_e= 236 cm^{-1}	
$\langle S^2 \rangle$= 2.040	$\langle S^2 \rangle$= 6.005	$\langle S^2 \rangle$= 2.014
$T_{e,\text{QCISD}}$= 0.0 eV	$T_{e,\text{QCISD}}$= 0.949 eV	$T_{e,\text{QCISD}}$= 0.825 eV
Q^{NPA}(Si)= −0.870 e	Q^{NPA}(Si)= −0.895 e	Q^{NPA}(Si)= −0.715 e
QCISD(T)/6-311++G($2d,2f$)	QCISD(T)/6-311++G($2d,2f$)	QCISD(T)/6-311++G($2d,2f$)
$E_{\text{QCISD(T)}}= -1928.307\,359^{\text{a}}$	$E_{\text{QCISD(T)}}= -1928.267\,148^{\text{a}}$	$E_{\text{QCISD(T)}}= -1928.265\,514^{\text{a}}$
$T_{e,\text{QCISD(T)}}$= 0.0 eV	$T_{e,\text{QCISD(T)}}$= 1.094 eV	$T_{e,\text{QCISD(T)}}$= 1.139 eV

[a]Optimized at QCISD/6-311++G(d,f).

tion theory (MP2),[10] and quadratic configuration interaction methods including all single- and double-excitation (QCISD).[11] The energies of the lowest electronic states were then refined at the higher QCISD(T)/6-311++G($2d,2f$) 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).[12] All calculations were carried out with the GAUSSIAN 94[13] suite of programs and core orbitals were (Si $1s$-$2p$ and Cu $1s$-$3p$) were frozen in all correlated calculations; the Cu d electrons were included, not frozen.

Because some states (e.g., the $^2\Sigma^+$ and $^2\Delta$) 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)[14,15] using the ANO basis set of Pierloot *et al.*[16] within the MOLCAS-3 program.[17]

The CASSCF/MRCISD energies were corrected by the Davidson method[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 $3d$ 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$^+$, and SiCu$^-$ are presented in Table I. The dissociation energies for SiCu, SiCu$^+$, and SiCu$^-$ and the ionization potential and electron affinity for SiCu are summarized in Table II.

A. SiCu

We studied what are probably the three lowest electronic states: $^2\Pi_r(1\sigma^2 1\delta^4 \pi^4 2\sigma^2 3\sigma^2 2\pi^1)$, $^4\Sigma^-(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2)$, $^2\Pi_i(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2; 3\sigma^0 2\pi^3)$ at the B3LYP, MP2, and QCISD levels of theory. The $^2\Delta[1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 (2\pi_x^2 - 2\pi_y^2)]$ and $^2\Sigma^+[1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 (2\pi_x^2 + 2\pi_y^2)]$ states were examined at the CASSCF/MRCISD level of theory because of their intrinsically multideterminential 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 $^2\Pi_r$ 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 ($\approx$336 cm^{-1}) and dissociation energies ($\approx$1.8 eV). In this state, we find the unpaired spin density to be located completely on the silicon atom, we find it to be very ionic ($\mu_e = 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($2d,2f$) level of theory. This state is more ionic ($\mu_e = 3.3$ 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 [$\sim$3.2 eV at QCISD(T)/6-311++G($2d,2f$)] in energy, is even more ionic ($\mu_e = 3.4$ D) and does lie in the region where Scherer *et al.*[1] 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 ($^2\Pi$) has the same symmetry. To more carefully examine this possibility we performed CASSCF/MRCISD calculations for the second and third roots of $^2\Pi$ symmetry (the $^2\Pi_r$ ground state being the first root). The second root was found to be very multiconfigurational, to have the dominant $C(2\sigma^2 3\sigma^\alpha 4\sigma^\alpha 2\pi^\beta) = 0.72$ 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 $C(2\sigma^2 3\sigma^1 4\sigma^0 2\pi^3) = 0.63$ configuration in the MRCISD expansion, and has a minimum at $r_e = 2.41$ Å with the harmonic frequency of 209 cm^{-1}. As for the $^2\Pi_r$ ground state,

TABLE II. Energetic properties (in eV) of SiCu, SiCu$^+$, and SiCu$^-$.

	D_e(SiCu)	IE_a(SiCu)	EA_a(SiCu)	D_e(SiCu$^+$)	D_e(SiCu$^-$)
B3LYP[a]	2.043	7.246	1.475	2.836	2.193
MP2[a]	1.783	6.874	1.325	2.165	2.054
QCISD[a]	1.830	6.744	1.222	2.270	2.036
QCISD(T)[b]	1.787	7.009	1.424	2.158	2.034

[a]Using 6-311++G(d,f) basis sets.
[b]Using 6-311++G($2d,2f$) basis sets at QCISD/6-311++G(d,f) geometry.

we expect that this bond length is too long because Cu $3d$ electron correlation is neglected. However, the excitation energy from the $^2\Pi_r$ 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 multideterminental based CASSCF ($4a_1$, $2b_1$, $2b_1$, $1a_1$ active space within C_{2v} symmetry) method to treat the $^2\Sigma^+$ and $^2\Delta$ states. After so doing and using the CASSCF/MRCISD(Q) energy for the $^2\Pi_r$ 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 $^2\Pi_r$ state.

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

$$^2\Pi_r \rightarrow {}^4\Sigma^- \quad 0.5 \text{ eV}$$

$$^2\Pi_r \rightarrow {}^2\Delta \quad 1.2 \text{ eV}$$

$$^2\Pi_r \rightarrow {}^2\Sigma^+ \quad 1.8 \text{ eV}$$

$$^2\Pi_r \rightarrow {}^2\Pi_i \quad 3.2 \text{ eV}$$

B. SiCu$^+$

We studied three low-lying cation electronic states: $^1\Sigma^+(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0)$, $^3\Pi_r(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^1)$, and $^3\Sigma^-(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^2)$ 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 ($2d,2f$) 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 $^3\Pi_r$ 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 $^1\Sigma^+$ state is reasonably well established to be the ground electronic state of SiCu$^+$.

C. SiCu$^-$

We studied six low-lying anion electronic states $^3\Sigma^-(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2)$, $^3\Pi_i(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^3)$, $^1\Sigma^+$ $(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^0 2\pi^4)$, $^1\Sigma^+(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^0 4\sigma^2)$, $^3\Pi_r(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^1 4\sigma^1)$, and $^5\Sigma^-(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^1 2\pi^2 4\sigma^1)$ derived using double occupancy for the $3d$ orbitals of Cu as well as for the bonding 2σ-MO with the four other valence electrons distributed throughout the 3σ, 4σ, and 2π valence orbitals. The $^1\Sigma^+(1\sigma^2 1\delta^4 1\pi^4 2\sigma^2 3\sigma^2 2\pi^2)$ 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($2d,2f$) level of theory (see Table II). Our calculated harmonic frequency (283 cm^{-1}) and dissociation energy into the lowest energy asymptote Si$^-(^4S)$+Cu(^2S) (D_e=2.04 eV) both suggest strong bonding in the ground state of SiCu$^-$.

$^5\Sigma^-$ and $^3\Pi_r$ states arising from promoting one electron from the 3σ-MO into the 4σ-MO and promoting one electron from the 2π-MO into the 4σ-MO, respectively, are the lowest excited state with 1.09 and 1.14 eV excitation energies. Three other states $^1\Sigma^+$, $^1\Sigma^+$, and $^3\Pi_i$ 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 2π-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 $^2\Pi_r$ ground state, not the $^2\Sigma$ state suggested earlier. In light of these findings, the analogous CRLAS studied 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 Møller–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$^-$ at QCISD(T)/6-311+G* level of theory. The calculated molecular parameters at this level of theory: r_e=2.235 Å and ω_e=325 cm^{-1} for SiCu ($^2\Pi_r$); r_e=2.258 Å and ω_e=311 cm^{-1} for SiCu$^+$ ($^1\Sigma^+$) and r_e=2.268 Å and ω_e=270 cm^{-1} for SiCu$^-$ ($^3\Sigma^-$) are very close to those found at the QCISD/6-311+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.

[1] J. J. Scherer, J. B. Paul, C. P. Collier, and R. J. Saykally, J. Chem. Phys. **102**, 5190 (1995).

[2] A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).

[3] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).

[4] A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).

[5] P. J. Hay, J. Chem. Phys. **66**, 4377 (1977).

[6] K. Raghavachari and G. W. Trucks, J. Chem. Phys. **91**, 1062 (1989).

[7] T. H. Dunning, Jr. and P. J. Hay, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1976), pp. 1–28.

[8] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[9] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[10] J. A. Pople, R. Seeger, and R. Krishnan, Int. J. Quant. Chem. Symp. **11**, 149 (1977).

[11] J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. **87**, 5968 (1987).

[12] H. B. Schlegel, J. Chem. Phys. **84**, 4530 (1984).

[13] GAUSSIAN 94 (Revision A1), M. J. Frisch, G. M. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1995.

[14] (a) K. Andersson, P.-A. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolonski, J. Phys. Chem. **94**, 5483 (1990); (b) K. Andersson, P.-A. Malmqvist, and B. O. Roos, J. Chem. Phys. **96**, 1218 (1992).

[15] (a) B. O. Roos, Chem. Phys. Lett. **15**, 153 (1972); (b) I. Shavitt, Int. J. Quantum Chem. Symp. **11**, 131 (1977), **12**, 5 (1978); (c) P. E. M. Siegbahn, J. Chem. Phys. **72**, 1647 (1980).

[16] K. Pierloot, B. Dumez, P.-O. Widmark, and B. O. Roos, Theor. Chim. Acta **90**, 87 (1995).

[17] MOLCAS Version 3, K. Anderson, M. R. A. Blomberg, M. P. Fulscher, V.

Kello, R. Lindh, P.-A. Malmqvist, J. Noga, J. Olsen, B. O. Roos, A. J. Sadlej, P. E. M. Siegbahn, M. Urban, and P.-O. Widmark, University of Lund, Sweden, 1994.

[18] E. R. Davidson, in *The World of Quantum Chemistry*, edited by R. Daudel (Reidel, Dortrecht, 1974), p. 17.

[19] S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. **8**, 61 (1974).

[20] J. J. Scherer, J. B. Paul, C. P. Collier, and R. J. Saykally, J. Chem. Phys. **103**, 113 (1995).

[21] J. J. Scherer, J. B. Paul, C. P. Collier, and R. J. Saykally, J. Chem. Phys. **103**, 9187 (1995).

[22] A. I. Boldyrev and J. Simons, Mol. Phys. **92**, 365 (1997).

[23] A. I. Boldyrev and J. Simons, *Periodic Table of Diatomic Molecules. Part A: Diatomics of Main Group Elements. Part B: Diatomics Composed of One Main Group Element and One Transion Metal Atom. Part C: Diatomics of Transition Metals* (Wiley, London, 1997).