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Multireference coupled-pair approximation study of the CuSi molecule

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Abstract. The electronic structure of the CuSi molecule was examined using the multireference coupled pair-approximation (MRCPA) following multireference single and double excitation configuration interaction calculations. We found the ground state to be the $^2\Pi$ state, and we evaluated the bond length, dissociation energy, vibrational frequency, and dipole moment for the $^2\Pi$ ground state and for low-lying $^4\Sigma^-$ and $^2\Delta$ excited states. The dissociation energy of the $^2\Pi$ ground state by MRCPA is 2.13 eV, which agrees well with the experimental value of 2.26 eV. The inclusion of higher excitations by MRCPA significantly improves the description of the bonding and the accuracy of the spectroscopic constants.

Key words: Multireference coupled-pair approximation – Multireference single and double excitation configuration interaction – Spectroscopic constants – Dissociation energy

1 Introduction

The nature of the bonding between Si and transition metal atoms is of great interest [1–7] because these interfaces [1, 5] and silicides [2–4] are technologically important in electronic devices. Special interest has been focused on Cu because of the potential use of Cu for ultra-large-scale integration metallization [2]. The Cu-Si interaction of Cu deposited on a Si surface [6, 7] and that of copper silicide in the bulk phase [3, 4] have been studied extensively. It is well known that Cu penetrates Si and silicon oxide surfaces and then diffuses rapidly into the bulk [6]. The CuSi molecule itself, on the other hand, has been little studied even though an understanding of diatomic molecules containing a Si atom and a transition metal is surely important for fundamental knowledge of silicides and interfaces. So far only two spectroscopic measurements [8, 9] and one ab initio molecular orbital (MO) calculation [10] using pseudo-potentials have been reported. According to a thermal experiment [8] in which the vapor phase of a Cu-Si alloy was studied, the dissociation energy D_e of the CuSi molecule is 217.7 ± 6.1 kJ/mol (2.256 ± 0.063 eV). Another experiment [9] in which rotationally resolved vibronic bands were measured, obtained the bond length R_e and vibrational frequency ω_e for the ground state and an excited state. Surprisingly, however, the electronic ground state has not yet been identified. In the latter experimental work [9], the electronic ground state was assumed to be the $^2\Sigma$ state based on an analogy to the $^1\Sigma^+$ ground state of the NiSi molecule predicted by theoretical studies [11, 12]. The previous MO calculation on CuSi concluded that the ground state is the $^2\Pi$ state [10], but the reliability of the calculation is insufficient because the basis set used was very simple, i.e., a $(8s7p6d)/[6s4p3d]$ set for the $3s$, $3p$, $3d$, and $4s$ shells of Cu, and further only a self-consistent-field (SCF) configuration was used as a reference configuration in the single and double excitation configuration interaction (SDCI) calculations. A more extensive calculation is desirable to identify the ground state of the CuSi molecule and to examine the nature of the bond.

A general consideration of the bonding nature of the CuSi molecule in its ground state is given here. The electronic ground state of the Si atom is ^3P ($3s^2 3p^2$), while the Cu atom has the ^2S ($3d^{10}4s^1$) ground state. The ground state of the CuSi molecule is thus considered to dissociate to the Cu (^2S) + Si (^3P) ground-state atomic asymptote. Photoemission experiments and band calculations on bulk copper disilicide show that the density of the non-bonding d states is quite large [3, 4] and the d band is fully occupied [3]. Thus, for the CuSi molecule,

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arrangements of only five valence electrons originating from the Cu 4s and the Si 3s and 3p result in four candidates for the ground state: $^2\Sigma^+$ and $^2\Delta$ (both $\sigma^2\sigma^1\pi^2$ in low-spin coupling), $^4\Sigma^-$ ($\sigma^2\sigma^1\pi^2$ in high-spin coupling), and $^2\Pi$ ($\sigma^2\sigma^2\pi^1$). Although all d orbitals are fully occupied, the 3d electrons significantly contribute to stabilize the bonding in the CuSi molecule as in other molecules including a Cu atom, for example, CuAl [12–15], CuLi [13], CuO [16, 17], CuS [16, 17], and Cu_2 [18–20]. We therefore need to take account of the 3d correlation to obtain reasonable estimates of the spectroscopic constants [12, 14, 16, 18, 20]. Furthermore, the coupled-pair functional (CPF) calculations on Cu_2 [19, 20] and CuX (X = O, S) [16] indicate that the inclusion of excitations higher than single and double significantly increases D_e and decreases R_e.

In the work described in this paper, we investigated the electronic structure of the CuSi molecule by using very accurate ab initio calculations. We used multireference single and double excitation CI (MRSDCI) with the complete active space SCF (CASSCF) MOs and the multireference coupled-pair approximation (MRCPA) developed by Tanaka and coworkers [21, 22], and we used extended basis sets in these calculations. Here we classify the ground state of the CuSi molecule and discuss the electronic structure as well as the spectroscopic constants, R_e, D_e, and ω_e, and the dipole moment evaluated for the ground and low-lying excited states.

2 Calculation methods

Previous calculations on relatively small molecules containing transition metal atom(s) [11–20] indicate that rather extensive basis sets including polarization and/or correlation functions are needed in order to account for the angular correlation of the d electrons. The basis set used for Cu in this study was derived from the atomic natural orbital set proposed by Bauschlicher [23].[1] We further added two s and one p diffuse functions whose exponents were obtained by multiplying the exponent of the outermost primitive function by 1/3 and 1/9 for s (ζ_s = 0.01208889, 0.00402963) and by 1/3 for p (ζ_p = 0.0183333). The final Cu basis set was of the form $(22s16p10d6f4g)/[9s7p4d3f2g]$. For Si we used the aug-cc-pVTZ set proposed by Woon and Dunning [24][1].

Preliminary CASSCF calculations were carried out to prepare the MO sets for the following MRSDCI calculations and to select the reference configuration state functions (CSFs). Because of the large angular correlation that results from the near degeneracy of the 4s and 4p orbitals of Cu [18], the CASSCF MOs were required for the successive MRSDCI calculations [14, 22]. In this procedure the active space consisted of eight orbitals that originated from the Cu 4s and 4p and from the Si 3s and 3p orbitals, and five valence electrons were distributed among these orbitals. According to the CASSCF results, the $^2\Pi$ state was the lowest energetically at any distance, but the lowest $^4\Sigma^-$ state lay slightly above the $^2\Pi$ state. Thus the $^2\Pi$ state appears to be the ground state, but the $^4\Sigma^-$ state must nonetheless be examined in detail because it remains a possible candidate for the ground state. The $^2\Delta$ state lay about 1 eV higher than the $^4\Sigma^-$ state, and the $^2\Sigma^+$ state lay further above the $^2\Delta$ state; therefore we did not consider the $^2\Sigma^+$ state as a candidate for the ground state.

The MRSDCI calculations were performed for the three lowest states, the $^2\Pi$, $^4\Sigma^-$, and $^2\Delta$ states, using their respective CASSCF

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[1] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 1.0, at the internet address http://emsp.pnl.gov:2080/forms/basisform.html.

natural orbitals. In this procedure all Cu 3d electrons as well as the five valence electrons were correlated. The reference configurations in the MRSDCI were selected from the CASSCF wavefunction, in which the absolute values of the coefficients were greater than 0.1 for each state. One, two and three reference configurations were used for the $^4\Sigma^-$, $^2\Delta$, and $^2\Pi$ states respectively, (denoted as 1RSDCI, 2RSDCI, and 3RSDCI). In these three MRSDCI calculations, the total weight of the reference(s) was larger than 90% at any distance, even though 1RSDCI calculations used only one reference. All calculations were carried out in C_{2v} symmetry for $^2A_1$ ($^2\Delta$ and/or $^2\Sigma^+$), $^4A_2$ ($^4\Sigma^-$), and $^2B_1$ ($^2\Pi$). For the $^2\Pi$, $^4\Sigma^-$ and $^2\Delta$ states, the total numbers of CSFs in MRSDCI were about 573 000, 441 000, and 383 000, respectively.

As is well known, the quality of the truncated (not full) CI calculations deteriorates as the number of correlated electrons increases [21, 22]. We estimated the contributions of quadruple excitation to the MRSDCI energy by using Davidson's scheme [25], and the results obtained by this scheme are denoted by +Q. To obtain more reliable results, we applied MRCPA [21, 22] to the $^2\Pi$ and $^4\Sigma^-$ states (denoted 3RCPA and 1RCPA, respectively). The MRCPA method sometimes overestimates the weight of single excitations in the valence space, and this makes it difficult to obtain well-converged results. We included such single excitation configurations in the model space on MRCPA in 3RCPA and 1RCPA calculations.

In evaluating the total energy of the dissociation limit (the Cu ^2S + Si ^3P asymptote), we used the high-spin state of the supermolecule with a nuclear distance of 100 a.u. In this calculation, only a SCF configuration could be used as the reference CSF in SDCI and CPA calculations. Calculations by MRCPA were done using the code developed by Tanaka and coworkers [21], while the ALCHEMY II program [26] was used for all other calculations.

3 Results and discussion

3.1 The $^2\Pi$ ground state

MRSDCI (and +Q) calculations of the three states (i.e., 3RSDCI, 1RSDCI, and 2RSDCI of the $^2\Pi$, $^4\Sigma^-$, and $^2\Delta$ states, respectively) and MRCPA calculations of the $^2\Pi$, and $^4\Sigma^-$ states (i.e., 3RCPA and 1RCPA, respectively) gave the lowest energy for the $^2\Pi$ state, which supports the previous simple calculation [10]. For instance, the MRSDCI +Q at a distance of 4.25 a.u. (near R_e of the $^2\Pi$ state) shows that the $^4\Sigma^-$ and $^2\Delta$ states are 0.40 and 1.48 eV higher than the $^2\Pi$ state respectively. The adiabatic excitation energy from the $^2\Pi$ state to the $^4\Sigma^-$ state is estimated to be 0.31, 0.40, and 0.66 eV by MRSDCI, MRSDCI+Q, and MRCPA(4) which is the fourth-order approximation in the MRCPA scheme. These results suggest that the ground state is the $^2\Pi$ state. The values of R_e, D_e, ω_e, and the dipole moment μ for the $^2\Pi$ ground state evaluated by CASSCF, 3RSDCI, 3RSDCI+Q, and 3RCPA(4) are listed in Table 1.

In the 3RSDCI calculations the reference configurations used were $10\sigma^2 11\sigma^2 5\pi x^1$ (configuration 1), $10\sigma^2 12\sigma^2 5\pi x^1$ (configuration 2), and $10\sigma^2 5\pi x^1 5\pi y^2$ (configuration 3). Among these configuration 1 is dominant, i.e., the CI coefficient is 0.93 at a distance of 4.25 a.u. (near R_e). The 10σ MO is essentially atomic Si 3s, and the 11σ and 12σ are the bonding and antibonding MOs between the Cu 4s and the Si $3p\sigma$, respectively. The open-shell 5πMO is mostly the Si $3p\pi$ orbital. Thus the chemical bonding in the $^2\Pi$ ground state arises qualitatively from a single σ bond [8] between the Cu 4s and the Si $3p\sigma$ electrons, and π electrons contribute little to the

Table 1. Spectroscopic constants of the $^2\Pi$ state

	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	μ (D)
CASSCF	> 2.43	> 0.98		
3RSDCI	2.283	1.59	303.6	2.71
3RSDCI + Q	2.258	1.79	310.2	
3RCPA(4)	2.265	2.13	312.9	2.42
2RSDCI	2.296	1.50	287.8	2.66
2RSDCI + Q	2.26<	> 1.74		
2RCPA(4)	2.314	1.73	268.5	2.43
5RSDCI	2.287	1.58	291.5	2.73
5RSDCI + Q	2.262	1.81	308.5	
Other calculations[a]				
SDCI + Q	2.30	1.51[b]	309	
CEPA-1		1.99[b]		
exp1[c]	2.34	2.26 ± 0.06	398	
exp2[d]	2.298		330 ± 15	

[a] Results with the $(8s7p6d)/[6s4p3d]$ set using the 19-valence-electron pseudopotential for Cu. See Ref. [10]
[b] Results with the $(8s7p6d2f)/[6s4p3d2f]$ set using the 19-valence-electron pseudo-potential for Cu. See Ref. [10]
[c] See Ref. [8]
[d] See Ref. [9]

bonding in the CuSi molecule. R_e given by CASSCF was larger than 2.43 Å, and R_e is shortened drastically by taking into account the electron correlation, especially that of the Cu $3d\pi$ electrons [18]; that is, 3RSDCI, 3RSDCI + Q, and 3RCPA(4) gave R_e values of 2.283, 2.258, and 2.265 Å, respectively. ω_e given by 3RSDCI is 303.6 cm^{-1}, and slightly larger values of 310.2 and 312.9 cm^{-1} are given by 3RCI + Q and 3RCPA(4), respectively. The value of D_e given by 3RSDCI was 1.59 eV, while the values given by 3RSDCI + Q and 3RCPA(4) were 1.79 eV and 2.13 eV, respectively. This result demonstrates that precise inclusion of higher excitations by MRCPA is effective in increasing D_e.

The dipole moments were evaluated using an 3RSDCI or 3RCPA wavefunction at the R_e of the respective approximation. The CuSi molecule in the $^2\Pi$ ground state has a polarity of $Cu^{\delta+}Si^{\delta-}$ at any level of calculation. The value of μ obtained by 3RCPA(4), 2.42 D, is smaller than that obtained by 3RSDCI, i.e., 2.71 D. This is in accord with the CPF result for CuO [16], in which the inclusion of higher excitations reduces the net charge on Cu and thus results in a smaller μ than is given by CI. In the 3RCPA wavefunction there are non-negligible contributions (the absolute value of the coefficient is greater than 0.01 but is less than 0.05) from some of the CSFs characterized as a single excitation from the Cu $3d$ orbitals. This is also consistent with previous CPF calculations of CuO [16] and Cu_2 [19], in which large decreases (compared with the CI result) in the d population occur at the CPF level.

To evaluate the reliability of these three-reference correlation calculations, we carried out 2R and 5R calculations. The results denoted as 2RSDCI [and 2RCPA(4)] and 5RSDCI respectively, are reported in Table 1. In the 2R calculations configuration 3 was excluded from the 3R space, but proper dissociation of the wavefunction was guaranteed by the remaining two reference configurations. The spectroscopic constants obtained differ significantly from those given by the corresponding 3R calculations. For instance, 2RSDCI

and 2RCPA(4) give a remarkably larger R_e, about 2.30 Å, than 3R calculations, but R_e given by 2RSDCI + Q is less than 2.26 Å. Furthermore, since the total weight of the references is less than 90% in the 2RSDCI wavefunction at any distance, + Q correction may not be reliable. The 2R treatment is unsatisfactory for describing the ground state. In the 5R calculations we added two configurations to the 3R space, $(10\sigma^0)11\sigma^2 5\pi x^1 5\pi y^2$ (configuration 4) and $10\sigma^1 11\sigma^1 5\pi x^1 5\pi y^1 6\pi y^1$ (configuration 5), where the 6π orbital consists of the $3p$ and $3d$ orbitals of Si and the $4p$ and $3d$ orbitals of Cu. These configurations are characterized by excitation(s) from the Si $3s$. Each configuration had a coefficient greater than 0.07 in the CASSCF calculation, and all five CSFs derived from configuration 5 were treated as reference CSFs. The total number of CSFs for 5RSDCI was about 199 2000. We did not perform 5RCPA because it was too time consuming. In the calculation of the dissociation limit, a configuration which is a double excitation from the $3s$ to $3p$ in Si was added to the reference in order to ensure consistency with 5R calculations. The resultant spectroscopic constants (Table 1) given by 5RSDCI and 5RSDCI + Q have magnitudes similar to those given by 3RSDCI and 3RSDCI + Q, though R_e is slightly longer and ω_e is slightly smaller. The D_e value given by 5RSDCI + Q is only slightly larger than that given by 3RSDCI + Q. This suggests that increasing the number of reference functions is less effective in improving D_e. These results indicate that the present 3R results are reliable.

The experimental spectroscopic constants of the ground state [8, 9] and the results of the previous calculation for the $^2\Pi$ state [10] are also included in Table 1. The D_e value for the $^2\Pi$ ground state estimated by 3RCPA(4), which is the most reliable calculation in this study, is 2.13 eV, and agrees satisfactorily with the experimental value of 2.26 ± 0.06 eV [8]. The best value of D_e among the previous calculations [10] was 1.99 eV given by the coupled-electron pair approximation (CEPA-1), which accounts for higher excitations but is used with only a single reference function. The R_e value for the $^2\Pi$ ground state obtained by 3RCPA(4) is 2.265 Å, which is slightly shorter than the experimental value of 2.298 Å [9] and the previous SDCI + Q [10] result, and it is different from another experimental value 2.34 Å [8]. 3RCPA(4) gives ω_e as 312.9 cm^{-1}, and the previous SDCI + Q yielded a similar value [10]. These values agree well with the experimental value of 330 ± 15 cm^{-1} [9], but are smaller than another experimental value of 398 cm^{-1} [8]. It is desirable to reexamine R_e and ω_e for the CuSi molecule in the ground state experimentally. To distinguish the ground state from other low-lying states, we think that measurement of the dipole moment would be helpful because μ of the $^2\Pi$ ground state is quite different from those of the $^4\Sigma^-$ and $^2\Delta$ states as discussed in Sect. 3.2

3.2 $^4\Sigma^-$ and $^2\Delta$ states

The values of R_e, D_e, ω_e, and μ for the $^4\Sigma^-$ and $^2\Delta$ states obtained in the present work and the previous SDCI

Table 2. Spectroscopic constants of the $^4\Sigma^-$ and $^2\Delta$ states

	R_e (Å)	D_e (eV)	ω_e (cm^{-1})	μ (D)
$^4\Sigma^-$ state				
CASSCF	> 2.43	> 0.88		
1RSDCI	2.252	1.28	297.2	4.51
1RSDCI + Q	2.230	1.39	310.6	
1RCPA(4)	2.220	1.47	320.3	3.78
3RSDCI	2.249	1.41	300.0	4.51
3RSDCI + Q	2.227	1.46	305.3	
Other calculations[a]				
SDCI + Q	2.29	1.17[b]	285	
$^2\Delta$ state				
CASSCF	> 2.43	> −0.66[c]		
2RSDCI	2.22	0.14[c]	375	4.19
2RSDCI + Q	2.26	0.32[c]	323	

[a] The same as in Table 1
[b] The same as in Table 1
[c] The dissociation energy was evaluated relative to the dissociation limit of the Cu ^2S + Si ^3P asymptote

results for the $^4\Sigma^-$ state [10] are summarized in Table 2. The reference configuration $10\sigma^2 11\sigma^1 5\pi x^1 5\pi y^1$ was used in the 1RSDCI calculations for the $^4\Sigma^-$ state. In 2RSDCI for the $^2\Delta$ sate the reference configurations were $10\sigma^2 11\sigma^1 5\pi x^2$ and $10\sigma^2 11\sigma^1 5\pi y^2$. The characteristics of these MOs are essentially similar to those of the $^2\Pi$ ground state. As inferred from these reference configurations, the $^4\Sigma^-$ and $^2\Delta$ states are rather ionic because in these states the π orbital, being mostly the Si 3p, is occupied by two electrons and the σ bonding orbital is half-occupied. This yields a smaller binding energy and a larger dipole moment for the $^4\Sigma^-$ and $^2\Delta$ states than for the $^2\Pi$ ground state.

The $^4\Sigma^-$ state has a slightly shorter R_e than the $^2\Pi$ ground state. The values of D_e for the $^4\Sigma^-$ state by 1RSDCI + Q and 1RCPA(4) are 1.39 and 1.47 eV, respectively, which are smaller than those for the $^2\Pi$ ground state. The reduction of μ by the higher excitations in MRCPA is also seen in 1RSDCI and 1RCPA(4) calculations for the $^4\Sigma^-$ state. For the $^4\Sigma^-$ state we carried out 3R calculations, similar to the 5R calculations for the ground state. In the 3R calculations, we added two double-excitation configurations: $10\sigma^1 11\sigma^2 5\pi x^1 6\pi y^1$ and $10\sigma^1 11\sigma^2 6\pi x^1 5\pi y^1$, which had coefficients greater than 0.08 in the CASSCF calculation. The total number of CSFs for 3RSDCI was about 130 2000, and we did not perform 3RCPA calculations. Table 2 shows that the spectroscopic constants obtained are similar to those obtained by the corresponding 1R calculations, suggesting that 1R treatment for the $^4\Sigma^-$ state is sufficient.

For the $^2\Delta$ state we did not perform MRCPA calculations. R_e of the $^2\Delta$ state is similar to that of the $^2\Pi$ ground and is slightly longer than that of the $^4\Sigma^-$ state. The larger ω_e for the $^2\Delta$ state than for the $^2\Pi$ and $^4\Sigma^-$ states indicates that the potential energy curve in the $^2\Delta$ state is a little steeper than that in the $^2\Pi$ and $^4\Sigma^-$ states.

4 Summary

MRCPA calculations following MRSDCI calculations were performed in order to investigate the electronic structure of the CuSi molecule. The ground state was found to be the $^2\Pi$ state. This state has a σ bond between the Cu 4s and Si 3$p\sigma$, and has a polarity of Cu$^{\delta+}$Si$^{\delta-}$. The $^4\Sigma^-$ and $^2\Delta$ states were found to lie about 0.7 eV and more than 1 eV above the ground state respectively, and were also found to be more ionic than the ground state. The inclusion of higher excitations by MRCPA significantly improves the bonding description, that is, MRCPA gave a D_e of 2.13 eV for the $^2\Pi$ ground state, which agrees well with the experimental value of 2.26 eV. We think it would be desirable to reexamine the other spectroscopic constants experimentally, as well as to measure a dipole moment to distinguish the $^2\Pi$ ground state from low-lying $^4\Sigma^-$ and $^2\Delta$ states.

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