

## The Molecular Structure and Ionization Potential of Si<sub>2</sub>: The Role of the Excited States in the Photoionization of Si<sub>2</sub>

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The ionization potentials (IP) of Si<sub>2</sub> (X <sup>3</sup>Σ<sub>g</sub><sup>-</sup>) to form the X <sup>4</sup>Σ<sub>g</sub><sup>-</sup> and a<sup>2</sup>Π<sub>u</sub> states of Si<sub>2</sub><sup>+</sup> have been calculated at very high levels of ab initio molecular orbital theory (CCSD(T) with augmented correlation-consistent basis sets extrapolated to the complete basis set limit). The calculated value of the IP to form the X <sup>4</sup>Σ<sub>g</sub><sup>-</sup> ground state of the ion is 7.913 eV as compared to an experimental value of 7.9206 eV. The a<sup>2</sup>Π<sub>u</sub> state is predicted to lie 0.52 eV above the X <sup>4</sup>Σ<sub>g</sub><sup>-</sup> ground state of Si<sub>2</sub><sup>+</sup>. The 1 <sup>3</sup>Δ<sub>u</sub>, 2 <sup>3</sup>Δ<sub>u</sub>, H <sup>3</sup>Σ<sub>u</sub><sup>-</sup>, and K <sup>3</sup>Σ<sub>u</sub><sup>-</sup> excited states of Si<sub>2</sub>, as well as the X <sup>4</sup>Σ<sub>g</sub><sup>-</sup>, a<sup>2</sup>Π<sub>u</sub>, and 2<sup>2</sup>Π<sub>u</sub> states of Si<sub>2</sub><sup>+</sup>, have been calculated at the multireference configuration interaction level. The agreement of the calculated positions of the states with the known experimental values is quite good (better than 0.1 eV). The calculated wave functions for the excited states of Si<sub>2</sub> show significant multireference character. This is especially true for the H state which has been used as an intermediate state in photoionization experiments. The multireference character of the H state readily allows the connection of this state to the ground X <sup>4</sup>Σ<sub>g</sub><sup>-</sup> electronic state of Si<sub>2</sub><sup>+</sup> via a one electron photoionization process.

### Introduction

The study of the structures and properties of small silicon clusters has been a very active area of research because of silicon's importance in both fundamental and applied science.<sup>1–11</sup> The discovery of emissive nanometer-scale silicon clusters has further heightened this interest.<sup>3</sup> Fundamental to the buildup of nanometer-size silicon clusters is an understanding of the underlying silicon–silicon interactions existing in the cluster which, to first order, are strongly influenced by the nature of the two-body Si–Si interaction (i.e., the silicon dimer bond). The ionization potential (IP) of the silicon dimer provides an important link in the understanding of the molecular electronic structure of the dimer, its chemical reactivity, and various dissociation processes. The IP also serves as a sensitive probe of the accuracy of theoretical calculations which extend from the evaluation of small silicon clusters to surface modeling.<sup>12,13</sup> Here we approach this description with chemically accurate calculations on the silicon dimer and its ion.

Si<sub>2</sub> has two low-lying states. The X <sup>3</sup>Σ<sub>g</sub><sup>-</sup> ground state, corresponding to an orbital occupancy of ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>2</sup>2π<sub>u</sub><sup>2</sup>, lies about 330 cm<sup>-1</sup> below the first excited state, of <sup>3</sup>Π<sub>u</sub> symmetry and ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>3</sup> occupancy. Both states have been the focus of high level calculations<sup>1,6</sup> and experimental measurements.<sup>1</sup> Given the closeness of the two neutral states, the ground state of the Si<sub>2</sub><sup>+</sup> cation could result from the removal of either a π or σ electron, resulting in a <sup>2</sup>Π<sub>u</sub> state

(...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>2</sup>2π<sub>u</sub><sup>1</sup>) or a <sup>4</sup>Σ<sub>g</sub><sup>-</sup> state (...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup>), respectively. It has been previously shown<sup>6</sup> at the G2 level<sup>14</sup> that the ground state of the ion is the <sup>4</sup>Σ<sub>g</sub><sup>-</sup> state, with the <sup>2</sup>Π<sub>u</sub> state lying 9.6 kcal/mol (0.42 eV) higher in energy.

There have been several experimental determinations of the IP of Si<sub>2</sub>. Trevor et al.<sup>10</sup> determined a lower bound of 7.87 eV, while Fuke et al.<sup>2</sup> determined the ionization energy to be higher than 8.49 eV. More recently, Boo and Armentrout<sup>9</sup> reported a value that was ≤8.04 eV, based on their measurement of the enthalpy of formation of Si<sub>2</sub><sup>+</sup> and the JANAF enthalpy of formation of Si<sub>2</sub>. Winstead et al.<sup>15</sup> used mass-selected resonant two-photon ionization spectroscopy through the H <sup>3</sup>Σ<sub>u</sub><sup>-</sup> state to bracket the IP between 7.9 and 8.08 eV, in good agreement with the results of Trevor et al. and Boo and Armentrout. Most recently, Marijnissen and ter Meulen<sup>16</sup> have used mass-selected photoionization spectroscopy through the intermediate N <sup>3</sup>Σ<sub>u</sub><sup>-</sup> (~...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup>5σ<sub>u</sub><sup>1</sup> in a single-determinant formalism) excited state of Si<sub>2</sub> to determine the adiabatic ionization energy of <sup>28</sup>Si<sub>2</sub> as 7.9206 eV. In the course of that study, the authors raised questions about the validity of the selected route for the two-photon ionization studies of Winstead et al., who accessed the intermediate H <sup>3</sup>Σ<sub>u</sub><sup>-</sup> (~...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>2</sup>2π<sub>u</sub><sup>1</sup>2π<sub>g</sub><sup>1</sup> in a single-determinant formalism) excited state of Si<sub>2</sub> in their bracketing experiment.

We have been developing computational chemistry methods to predict the energetics of a range of first- and second-row

molecules to chemical accuracy. Our approach does not rely on empirical corrections.<sup>17</sup> We have recently been calculating the thermodynamic properties of several silicon-containing molecules.<sup>17i</sup> Here, we report calculations on the spectroscopic properties and dissociation energies for the ground state and for several low-lying excited states of the Si<sub>2</sub> molecule relevant to the photoionization process. We also calculate the energies of the three lowest lying states of Si<sub>2</sub><sup>+</sup>. This study provides further confirmation of the ionization potential, the energetics of several excited states of Si<sub>2</sub> and the relative energetics of the three lowest states of the ion, and the optimal bond lengths of the considered states. In the present study, we also evaluate the conclusions of Marijnissen and ter Meulen<sup>16</sup> in light of the result that many of the low-lying states of Si<sub>2</sub> are not well described by a single configuration.

## Approach

Calculations on the ground state of Si<sub>2</sub> and on the two lowest lying states of Si<sub>2</sub><sup>+</sup> were carried out at the coupled cluster level of theory with single and double excitations and a perturbative correction for the triple excitations [CCSD(T)].<sup>18</sup> The initial energetics were calculated within the frozen core (FC) approximation in which the 10 inner shell electrons (1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>) on each silicon atom were excluded from the correlation treatment. When combined with large basis sets, the CCSD(T)(FC) level of theory is capable of recovering a significant fraction of the valence correlation energy. There are currently three widely used CCSD(T) approaches for handling open shell systems.<sup>19</sup> The calculations on the ions were done with ROHF orbitals, but with the spin constraint relaxed in the coupled cluster portion of the calculation. Energies obtained from this hybrid procedure are denoted R/UCCSD(T). The calculations for the neutral were done with unrestricted Hartree–Fock (UHF) orbitals, denoted as UCCSD(T). For Si<sub>2</sub> the UCCSD(T) and R/UCCSD(T) methods produce energies that agree to within 0.0001 E<sub>h</sub>. Spectroscopic constants were obtained via the usual Dunham<sup>20</sup> analysis using coefficients from polynomial fits in  $\Delta r = r - r_e$  for 6 to 7 points of each potential energy curve.

The orbitals for the multireference configuration interaction (MRCI) calculations were obtained as natural orbitals from complete active space self-consistent field (CASSCF) calculations with a full valence active space, i.e., all molecular orbitals arising from the valence atomic orbitals were included in the active space. The core orbitals were optimized, but constrained to be doubly occupied. In all cases for the neutral, a state average of five states was carried out corresponding to the <sup>3</sup>Σ<sub>g</sub><sup>-</sup> ground state, the two lowest lying <sup>3</sup>Δ<sub>u</sub> states, and the two lowest lying <sup>3</sup>Σ<sub>u</sub><sup>-</sup> states. The former were found to be relatively low-lying states in preliminary CCSD(T) calculations, and the latter were necessary for treating the H-state of the neutral. This common set of orbitals was then used in internally contracted<sup>21</sup> MRCI (icMRCI) calculations with a reference function identical to the CASSCF active space (292 configuration state functions). Only the valence electrons were correlated. In the icMRCI calculations, although the ground state was calculated separately, the four excited states were calculated simultaneously as the first four roots in A<sub>u</sub> symmetry (D<sub>2h</sub> symmetry was used throughout). A similar treatment was also used for the positive ion. The orbitals were obtained in a state-averaged CASSCF (X <sup>4</sup>Σ<sub>g</sub><sup>-</sup>, <sup>1</sup>Π<sub>u</sub>, and <sup>2</sup>Π<sub>u</sub>), and the MRCI calculations consisted of a separate calculation for the ground state and a two-state icMRCI for the <sup>2</sup>Π<sub>u</sub> states. The MRCI results were also corrected for higher order excitations through the use of the multireference Davidson “+Q” correction.<sup>22</sup> Spectroscopic constants were

TABLE 1: UCCSD(T)(FC) Results for Si<sub>2</sub> (X <sup>3</sup>Σ<sub>g</sub><sup>-</sup>)

basis	D <sub>e</sub> (kcal/mol)	R <sub>e</sub> (Å)	ω <sub>e</sub> (cm <sup>-1</sup> )	ω <sub>e</sub> x <sub>e</sub> (cm <sup>-1</sup> )	E (E <sub>h</sub> )
cc-pVDZ	60.93	2.2959	492.3	1.88	-577.927107
cc-pVTZ	70.31	2.2681	509.3	1.93	-577.977596
cc-pVQZ	73.61	2.2572	513.8	1.94	-577.991813
cc-pV5Z	74.98	2.2527	515.5	1.93	-577.996613
aug-cc-pVDZ	63.00	2.2958	491.5		-577.937001
aug-cc-pVTZ	71.12	2.2681	507.5		-577.980994
aug-cc-pVQZ	73.87	2.2564	515.9		-577.993292
aug-cc-pV5Z	75.01	2.2526	516.3		-577.997720
aug-cc-pV6Z	75.37	2.2519			-577.999191
CBS(aTQ5/exp)	76.18				-578.00021
CBS(aTQ5/mix)	75.61				-578.00030
CBS(aQ56/exp)	75.77				-578.00030
CBS(aQ56/mix)	75.58				-578.00005
expt <sup>a</sup>		2.246	510.98	2.02	

<sup>a</sup> Reference 29.

obtained via the usual Dunham analysis using coefficients from polynomial fits in  $\Delta r = r - r_e$  for 6 to 7 points of each potential energy curve.

All calculations were performed with the correlation consistent (cc-pVnZ or aug-cc-pVnZ) basis sets.<sup>23</sup> The geometries for the ions were optimized in a pointwise fashion with the normal cc-pVnZ basis sets for n = D, T, Q, and 5. Energies were also calculated with the diffuse function augmented sets, denoted aug-cc-pVnZ, at the cc-pVnZ geometry for the same n. For the neutral and in all MRCI calculations, the geometries were also optimized with the aug-cc-pVnZ basis sets. These sequences of basis sets have been extensively demonstrated to provide reliable thermochemical and structural properties, with rare exceptions.<sup>17</sup> Only the spherical components (i.e., 5-d, 7-f, 9-g, etc.) of the Cartesian basis functions were used.

All calculations were performed with the MOLPRO-96/97<sup>24</sup> and Gaussian 94<sup>25</sup> programs on Silicon Graphics PowerChallenge compute servers.

To estimate energies at the complete basis set (CBS) limit, we used a mixed exponential/Gaussian function of the form

$$E(n) = A_{\text{CBS}} + B \cdot \exp[-(n-1)] + C \cdot \exp[-(n-1)^2] \quad (1)$$

where n = 2 (DZ), 3 (TZ), etc., first proposed by Peterson et al.<sup>26</sup> We denote this as CBS(aTQ5/mix). As a crude handle on the likely error associated with the CBS extrapolation, we use the spread in the CBS estimates obtained from the mixed expression and a simple exponential:<sup>27</sup>

$$E(n) = A_{\text{CBS}} + B \cdot \exp(-Cn) \quad (2)$$

In the study of Feller and Peterson,<sup>17</sup> the mixed expression produced the smallest mean absolute deviation with respect to experiment by a small measure as compared to other extrapolation methods such as the simple exponential.

Having estimated energies at the CCSD(T)(FC)/CBS level of theory, we then include a number of additional corrections to account for core-valence, spin-orbit effects, and molecular scalar relativistic effects. Zero point vibrational energies are also evaluated. The frequencies for the ion were calculated with the cc-pVQZ basis set. Core-valence corrections to the dissociation energy were obtained from fully correlated CCSD(T) calculations with the cc-pCVTZ basis set<sup>36</sup> at the CCSD(T)/cc-pVTZ geometry. Experience has shown that the cc-pCVTZ basis set recovers ~75% or more of the effect seen with the larger cc-pCVQZ basis. A final correction to account for scalar relativistic effects is also applied. We evaluate the scalar relativistic correction using configuration interaction wave functions with

**TABLE 2: Details of the Calculation of  $D_e$  and the Ionization Potentials of  $\text{Si}_2^a$** 

molecule	CBS $D_e$	$1/2 \omega_e$ (aVQZ)	$\Delta E_{\text{CV}}^e$	$\Delta E_{\text{SR}}^f$	$\Delta E_{\text{SO}}^g$	$\Sigma D_0$	IP (eV)	expt
$\text{Si}_2$ ( $X^3\Sigma_g^-$ ) <sup>b</sup>	75.6	0.74	0.5	-0.1	-0.9	$74.4 \pm 0.4$		$74.0^h$
$\text{Si}_2^+$ ( $X^4\Sigma_g^-$ ) <sup>c</sup>	-106.59 <sup>d</sup>	0.68	0.2	-0.1	-0.9		$7.913$ ( $7.918$ ) <sup>j</sup>	$7.9206$ eV <sup>i</sup>
$\text{Si}_2^+$ ( $a^2\Pi_u$ ) <sup>e</sup>	-118.83 <sup>d</sup>	0.56	0.1	-0.1	-0.9		$8.443$ ( $8.444$ ) <sup>j</sup>	

<sup>a</sup> Results are given in kcal/mol except for the ionization potentials which are given in eV. The total theoretical value is defined as:  $E[\text{CCSD(T)(FC)/CBS}] - 1/2\omega_e + \text{CV} + \text{scalar relativistic} + \text{atomic/molecular SO}$ . <sup>b</sup> Calculated with the UCCSD(T) method. <sup>c</sup> Calculated with the R/UCCSD(T) method. <sup>d</sup> The negative value corresponds to the fact that  $\text{Si}_2^+$  is unbound relative to two ground state Si atoms. <sup>e</sup> Core-valence corrections were obtained with the cc-pwCVTZ basis set at the optimized CCSD(T)/aug-cc-pVTZ geometries. A positive sign indicates that CV effects increase the stability of the molecule relative to the atomic asymptotes. <sup>f</sup> The scalar relativistic correction is based on CISD(FC)/cc-pVTZ calculations of the 1-electron Darwin and mass-velocity terms evaluated at the CCSD(T)(FC)/aug-cc-pVTZ geometry. <sup>g</sup> Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. <sup>h</sup> Reference 29. <sup>i</sup> Reference 16. <sup>j</sup> First value is CBS(aTQ5/mix) and the value in parentheses is CBS(aTQ5/exp).

**TABLE 3:  $\text{Si}_2$  Results from MRCI Calculations on the Ground State and Selected Excited States<sup>a</sup>**

	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$E$ ( $E_h$ )	$\Delta E$ (eV)	$\Delta E$ (cm <sup>-1</sup> )
aug-cc-pVTZ						
$X^3\Sigma_g^-$	2.2743	500.2	2.01	-577.968512	0.000	0
+Q	2.2723	501.5	2.03	-577.984341	0.000	0
$1^3\Delta_u$	2.6316	312.3	1.79	-577.896568	1.958	15790
+Q	2.6255	315.1	1.74	-577.913743	1.921	15494
$2^3\Delta_u$	2.3581	365.7	3.26	-577.850753	3.204	25845
+Q	2.3552	373.6	2.87	-577.869482	3.125	25209
$H^3\Sigma_u^-$	2.7041	261.8	1.87	-577.85955	2.965	23914
+Q	2.6776	272.0	1.72	-577.87955	2.852	22999
$K^3\Sigma_u^-$	2.3823	430.1	7.15	-577.828112	3.820	30814
+Q	2.3669	417.6	3.03	-577.846379	3.754	30279
aug-cc-pVQZ						
$X^3\Sigma_g^-$	2.2638	505.5	2.01	-577.979582	0.000	0
+Q	2.2612	507.2	2.04	-577.996044	0.000	0
$1^3\Delta_u$	2.6183	317.0	1.71	-577.906383	1.992	16065
+Q	2.6116	320.0	1.64	-577.924144	1.956	15780
$2^3\Delta_u$	2.3410	376.0	2.56	-577.86096	3.228	26035
+Q	2.3374	385.2	2.16	-577.880325	3.149	25397
$H^3\Sigma_u^-$	2.6888	264.9	1.79	-577.868842	3.013	24305
+Q	2.6606	276.0	1.73	-577.889472	2.900	23390
$K^3\Sigma_u^-$	2.3700	447.0	8.05	-577.838503	3.839	30963
+Q	2.3526	437.6	5.33	-577.857473	3.771	30413
aug-cc-pV5Z						
$X^3\Sigma_g^-$	2.2597	507.4	1.99	-577.983431	0.000	0
+Q	2.2569	509.2	2.02	-578.000095	0.000	0
$1^3\Delta_u$	2.6123	320.1	1.69	-577.909694	2.006	16183
+Q	2.6053	323.3	1.65	-577.927663	1.971	15897
$2^3\Delta_u$	2.3341	380.7	2.38	-577.864302	3.242	26146
+Q	2.3303	390.2	1.99	-577.883895	3.162	25503
$H^3\Sigma_u^-$	2.6803	267.9	1.80	-577.87194	3.034	24469
+Q	2.6520	279.3	1.76	-577.892794	2.920	23550
$K^3\Sigma_u^-$	2.3644	453.5	8.23	-577.841986	3.849	31044
+Q	2.3466	445.5	6.09	-577.861206	3.779	30483
expt <sup>b</sup>						
$X^3\Sigma_g^-$	2.246	510.98	2.02		0	0
$H^3\Sigma_u^-$	2.6427	279.28	1.99		2.9945	24151
$K^3\Sigma_u^-$	2.348	462.6	5.95		3.8180	30792

<sup>a</sup> Rows labeled with +Q include the multireference Davidson correction. <sup>b</sup> Reference 29.

single and double excitations (CISD/cc-pVTZ).<sup>28</sup> Specifically, the scalar relativistic energy lowering is defined to be the sum of the expectation values of the 1-electron Darwin and mass-velocity terms in the Breit-Pauli Hamiltonian. Tests show this approach to be capable of reproducing scalar relativistic corrections obtained from more accurate methods to within about 0.1 kcal/mol.

## Results

The UCCSD(T) results for the ground state of  $\text{Si}_2$  are given in Tables 1 and 2. The multireference CI results for  $\text{Si}_2$  ( $X^3\Sigma_g^-$ ,

$1^3\Delta_u$ ,  $2^3\Delta_u$ ,  $H^3\Sigma_u^-$ , and  $K^3\Sigma_u^-$ ) are given in Table 3. The R/UCCSD(T) results for the two lowest states of the ion  $\text{Si}_2^+$  are given in Tables 2 and 4, while the MRCI results for  $\text{Si}_2^+$  are shown in Table 5.

The calculated bond length for ground-state  $\text{Si}_2$  using the aug-cc-pVQZ and higher basis sets are within 0.01 Å of the experimental value.<sup>29</sup> The remaining error is due primarily to core-valence correlation effects.<sup>37</sup> The frequencies calculated at the highest levels for the ground state are within 4 cm<sup>-1</sup> of the experimental values.<sup>29</sup> To calculate  $D_e$  for the ground state, we have included a correction for core-valence interactions of

**TABLE 4: R/UCCSD(T) Results for the X<sup>4</sup>Σ<sub>g</sub><sup>-</sup> and a<sup>2</sup>Π<sub>u</sub> States of Si<sub>2</sub><sup>+</sup>**

	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$E_{\min}$ (E <sub>h</sub> )	$E_{\min}$ (E <sub>h</sub> ) augmented
X <sup>4</sup> Σ <sub>g</sub> <sup>-</sup>					
cc-pVDZ	2.3140	455.7	2.33	-577.650659	-577.655747
cc-pVTZ	2.2850	470.4	2.64	-577.691624	-577.693434
cc-pVQZ	2.2734	475.5	2.40	-577.703324	-577.703927
cc-pV5Z	2.2704			-577.707103	-577.707443
CBS(TQ5/exp)	2.2668			-577.70891	-577.70922
CBS(TQ5/mix)				-577.70930	-577.70949
a <sup>2</sup> Π <sub>u</sub>					
cc-pVDZ	2.5095	371.9	1.57	-577.628929	-577.635128
cc-pVTZ	2.4692	392.9	2.05	-577.671272	-577.6733139
cc-pVQZ	2.4573	396.7	1.74	-577.683364	-577.684040
cc-pV5Z	2.4541			-577.687430	-577.687825
CBS(TQ5/exp)	2.4512			-577.68949	-577.68989
CBS(TQ5/mix)				-577.68979	-577.69003

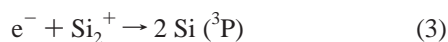
**TABLE 5: Si<sub>2</sub><sup>+</sup> Results from MRCI Calculations on the Ground State and Selected Excited States<sup>a</sup>**

	$r_e$ (Å)	$\omega_e$ (cm <sup>-1</sup> )	$\omega_e x_e$ (cm <sup>-1</sup> )	$E$ (E <sub>h</sub> )	$\Delta E$ (eV) <sup>b</sup>
aug-cc-pV5Z					
X <sup>4</sup> Σ <sub>g</sub> <sup>-</sup>	2.2742	471.8	2.49	-577.7013634	7.675
+Q	2.2745	470.1	2.52	-577.7107371	7.874
a <sup>2</sup> Π <sub>u</sub>	2.4546	385.3	1.55	-577.681062	8.228
+Q	2.4503	387.5	1.72	-577.692666	8.366
2 <sup>2</sup> Π <sub>u</sub>	2.2218	627.1	11.99	-577.652346	9.009
+Q	2.2162	607.2	7.45	-577.662566	9.185

<sup>a</sup> Rows labeled with +Q include the multireference Davidson correction. <sup>b</sup> Relative to the MRCI/aug-cc-pV5Z results for the ground state of the neutral. Zero-point vibrational energy corrections are not included.

0.5 kcal/mol, a scalar relativistic correction of -0.1 kcal/mol, and an atomic spin-orbit correction of -0.9 kcal/mol. The calculated values for  $D_0$  are likely to be more accurate than the available experimental ones. The CBS(aTQ5) and CBS(aQ56) values in Table 1 show that the basis set extrapolation is stable with respect to further increases in the 1-particle basis set. Spectroscopic measurements yield  $D_0 = 70 \pm 4$  kcal/mol, with an upper limit of  $D_0 = 74.0$  kcal/mol.<sup>30</sup> Knudsen cell/third law measurements on the Si-Si<sub>2</sub> equilibrium yield  $D_0$  values of 73.3, 74.3, and 70.4 kcal/mol (average = 72.7 kcal/mol).<sup>31</sup> The CCSD(T)/CBS value of  $D_0(\text{Si}_2) = 74.4 \pm 0.4$  kcal/mol calculated in this study is at the high end of these values<sup>30-32</sup> but in good agreement with the 74.0 kcal/mol, which is based on several experimental measurements, recommended by Huber and Herzberg.<sup>28</sup>

The contribution of the electronic energy to the adiabatic ionization potential for the ground state of Si<sub>2</sub> (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) is calculated to be 7.913 eV (182.48 kcal/mol) at the CBS(aTQ5/mix) level. A similar calculation at the CBS(aTQ5/exp) level yields 7.918 eV. Thus, there is a difference of only 0.005 eV between the two extrapolation methods. To calculate various correction factors to obtain the electronic energy of the ion, we have determined the “atomization energy” of Si<sub>2</sub><sup>+</sup> by the following process (note that it gives a negative  $D_e$ ):



With a core-valence correction of 0.013 eV (0.3 kcal/mol), a scalar relativistic correction of -0.010 eV (-0.2 kcal/mol), and a negligible neutral-ion zero point energy difference, we obtain a predicted IP of  $7.92 \pm 0.02$  eV for Si<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) to form Si<sub>2</sub><sup>+</sup>(X<sup>4</sup>Σ<sub>g</sub><sup>-</sup>). This value is in excellent agreement with the experimental value of 7.9206(9) eV.<sup>16</sup> The G2 value<sup>6</sup> of 7.94 eV for the X<sup>4</sup>Σ<sub>g</sub><sup>-</sup> state is in very good agreement with our calculated value at the CBS limit.

In a similar fashion, the electronic energy contribution to the adiabatic ionization potential for the a<sup>2</sup>Π<sub>u</sub> state is calculated to be 8.443 eV, with the two extrapolation procedures differing by only 0.001 eV. For the a<sup>2</sup>Π<sub>u</sub> state, the core-valence correction is 0.017 eV (0.4 kcal/mol), the scalar relativistic correction is -0.013 eV (-0.3 kcal/mol), and the zero point correction is -0.006 eV (0.13 kcal/mol). The predicted adiabatic IP for Si<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) to form Si<sub>2</sub><sup>+</sup>(a<sup>2</sup>Π<sub>u</sub>) is  $8.44 \pm 0.02$  eV. Thus, the a<sup>2</sup>Π<sub>u</sub> state of the cation is predicted to lie 0.52 eV above the X<sup>4</sup>Σ<sub>g</sub><sup>-</sup> state.

Because the calculated bond distance for the ground state of Si<sub>2</sub>, 2.255 Å, is very similar to the value predicted for the ground state of Si<sub>2</sub><sup>+</sup>(X<sup>4</sup>Σ<sub>g</sub><sup>-</sup>), 2.267 Å, the vertical and adiabatic ionization potentials will be very similar. However, the calculated bond distance for the Si<sub>2</sub><sup>+</sup> a<sup>2</sup>Π<sub>u</sub> state is significantly longer at 2.451 Å. Thus, vertical ionization to the a<sup>2</sup>Π<sub>u</sub> state is expected to require an additional 0.28 eV energy increment. We note that the G2 value<sup>6</sup> of 8.36 eV for the adiabatic IP of the a<sup>2</sup>Π<sub>u</sub> state is in reasonable agreement with our calculated value at the CBS limit.

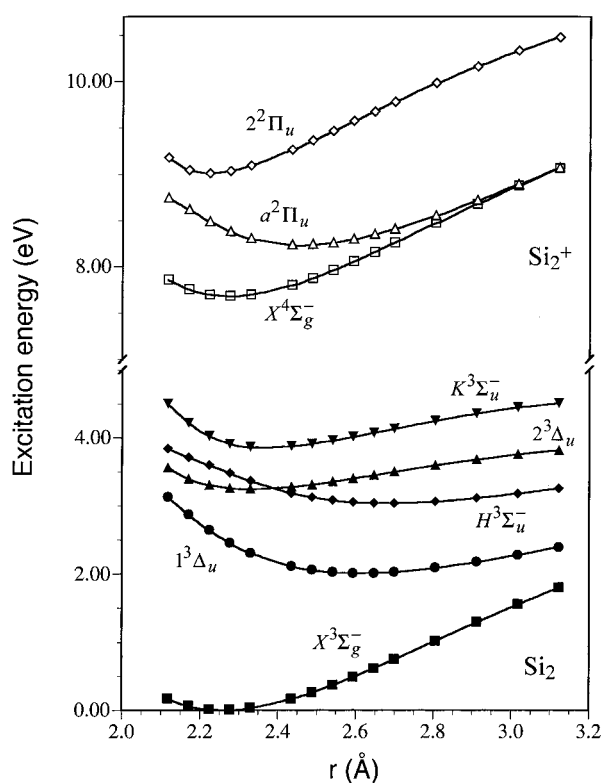
The calculated spectroscopic parameters for the excited 1<sup>3</sup>Δ<sub>u</sub>, 2<sup>3</sup>Δ<sub>u</sub>, H<sup>3</sup>Σ<sub>u</sub><sup>-</sup>, and K<sup>3</sup>Σ<sub>u</sub><sup>-</sup> states of Si<sub>2</sub> at the MRCI level with different correlation consistent basis sets are given in Table 3. Figure 1 presents the calculated potential energy curves. We note that the MRCI results without the +Q correction seem to yield values of  $\Delta E$  in somewhat better agreement with experiment than MRCI+Q by a few hundredths of an eV. However, the predicted bond distances seem to be predicted better with the +Q correction. For the calculations with the aug-cc-pV5Z basis set, the agreement with the experimentally determined values of  $r_e$ ,  $\omega_e$ ,  $\omega_e x_e$ , and  $T_e$  of the H and K states is, overall, excellent. At the MRCI level for the H state, the bond distance is within 0.04 Å,  $\omega_e$  within 11 cm<sup>-1</sup>, and  $\Delta E$  within 0.04 eV. At the MRCI+Q level, the bond distance is within 0.01 Å,  $\omega_e$  within 1 cm<sup>-1</sup>, and  $\Delta E$  within 0.07 eV. Thus, we are able to reliably reproduce the parameters of the H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> state. A similar high level of agreement is found for the K state with the geometry at the MRCI level now within 0.02 Å and both values for  $\Delta E$  within 0.04 eV. The results presented in Table 3 for the excited states of Si<sub>2</sub> are the most accurate available to date.

In Table 6, we summarize the dominant reference configurations for the calculated excited states of Si<sub>2</sub>. Not surprisingly, we note that the excited states of Si<sub>2</sub> have significant multireference character. This is especially true for the 2<sup>3</sup>Δ<sub>u</sub>, H<sup>3</sup>Σ<sub>u</sub><sup>-</sup>, and K<sup>3</sup>Σ<sub>u</sub><sup>-</sup> states. Our ability to accurately calculate the spectroscopic parameters of the H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> and K<sup>3</sup>Σ<sub>u</sub><sup>-</sup> states of Si<sub>2</sub> suggests that we have obtained very reliable descriptions of these multireference excited states. We especially note that the



**TABLE 6: Dominant Configurations for the Ground and Selected Excited States of  $\text{Si}_2$  Based on MRCI Calculations**

state		coefficient	excitation	configuration
$X^3\Sigma_g^-$	$r_e(X)$	0.913		$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^2$
		0.117	$2\pi_u^2 \rightarrow 2\pi_g^2$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_g^2$
$1^3\Delta_u$	vertical	0.891	$2\pi_u^2 \rightarrow 2\pi_u^1 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^1 2\pi_g^1$
		0.243	$5\sigma_g^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 2\pi_u^3 2\pi_g^1$
$2^3\Delta_u$	vertical	0.857	$5\sigma_g^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 2\pi_u^3 2\pi_g^1$
		0.236	$2\pi_u^2 \rightarrow 2\pi_u^1 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^1 2\pi_g^1$
		0.168	$5\sigma_g^2 2\pi_u^2 \rightarrow 2\pi_u^1 2\pi_g^3$	$4\sigma_g^2 4\sigma_u^2 2\pi_u^1 2\pi_g^3$
		0.163	$4\sigma_u^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 5\sigma_g^2 2\pi_u^3 2\pi_g^1$
		0.636	$2\pi_u^2 \rightarrow 2\pi_u^1 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^1 2\pi_g^1$
$H^3\Sigma_u^-$	vertical	0.608	$5\sigma_g^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 2\pi_u^3 2\pi_g^1$
		0.218	$5\sigma_g^2 \rightarrow 5\sigma_g^1 5\sigma_u^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^1 2\pi_u^2 5\sigma_u^1$
		0.778	$2\pi_u^2 \rightarrow 2\pi_u^1 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^1 2\pi_g^1$
$H^3\Sigma_u^-$	$\sim r_e(H)$	0.270	$5\sigma_g^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 2\pi_u^3 2\pi_g^1$
		0.362	$5\sigma_g^2 \rightarrow 5\sigma_g^1 5\sigma_u^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^1 2\pi_u^2 5\sigma_u^1$
		0.175	$5\sigma_g^2 2\pi_u^2 \rightarrow 5\sigma_g^1 5\sigma_u^1 2\pi_g^2$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^1 5\sigma_u^1 2\pi_g^2$
		0.651	$5\sigma_g^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 2\pi_u^3 2\pi_g^1$
		0.571	$2\pi_u^2 \rightarrow 2\pi_u^1 2\pi_g^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^2 2\pi_u^1 2\pi_g^1$
$K^3\Sigma_u^-$	vertical	0.211	$5\sigma_g^2 \rightarrow 5\sigma_g^1 5\sigma_u^1$	$4\sigma_g^2 4\sigma_u^2 5\sigma_g^1 2\pi_u^2 5\sigma_u^1$
		0.153	$4\sigma_u^2 2\pi_u^2 \rightarrow 2\pi_u^3 2\pi_g^1$	$4\sigma_g^2 5\sigma_g^2 2\pi_u^3 2\pi_g^1$

**Figure 1.** Ground and excited state curves for  $\text{Si}_2$  and  $\text{Si}_2^+$  calculated at the MRCI/aug-cc-pV5Z level of theory. Note that addition of the multireference Davidson correction (+Q) shifts the  $\text{Si}_2^+$  states by about +0.1 eV relative to the  $\text{Si}_2$  ground state.

multireference nature of the  $H^3\Sigma_u^-$  state is very dependent on the value of the internuclear distance  $r$ . The character of the wave function in the region near the minimum of this excited state is quite different from that predicted for the region which corresponds to the value of  $r_e$  for the ground state and thus the vertical Franck–Condon region. The multireference nature of the  $H^3\Sigma_u^-$  state has significant implications for the experimental determination of the  $\text{Si}_2$  ionization potential. We also note that the coefficients shown in Table 6 are not sensitive to our choice of state-averaged orbitals. For example, calculations employing orbitals separately optimized for the H state at its  $r_e$  yield MRCI coefficients for the three most dominant reference configurations of 0.79, 0.28, and 0.33 as compared to the state-averaged results shown in Table 6 of 0.78, 0.27, and 0.36. Such small differences

**TABLE 7:  $\text{Si}_2$   $H^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$  Dipole Transition Matrix Elements (in Debye) from MRCI Dipole Transition Moments and MRCI+Q Potential Energy Functions with the aug-cc-pV5Z Basis Set<sup>a</sup>**

$v'' \setminus v'$	0	1	2	3	4	5
0	-0.006	0.019	-0.044	0.081	-0.134	0.201
1	-0.023	0.066	-0.137	0.232	-0.346	0.467
2	-0.060	0.157	-0.292	0.446	-0.587	0.690
3	-0.125	0.295	-0.489	0.651	-0.730	0.698
4	-0.223	0.467	-0.671	0.747	-0.655	0.415
5	-0.353	0.640	-0.764	0.652	-0.341	-0.051

<sup>a</sup> The calculated dipole transition moment varies from 2.34 D at the X state  $r_e$  to 2.35 D at the H state  $r_e$ , with a maximum of about 2.64 D near  $r = 2.43$  Å.

have no impact on the qualitative discussion of the interactions of the various states as discussed below.

The dipole transition moments have also been calculated between the X and H states of the neutral using MRCI/aug-cc-pV5Z wave functions. Rotationless transition dipole moment vibrational matrix elements were then determined using numerical vibrational wave functions calculated<sup>35</sup> from the MRCI+Q potential energy functions. These results are shown in Table 7. Since the equilibrium bond length of the H state is significantly longer than that of the ground state, the largest matrix elements and hence Franck–Condon factors occur when the ground state and H state are in excited vibrational states. For transitions arising from  $v'' = 0$  of the ground electronic state, the largest matrix elements occur for  $v' > 5$ . This is in good agreement with the laser-induced fluorescence (LIF) results of Winstead et al., where the transitions shown for  $v'' = 0$  and  $v' = 5$  were more intense than those with smaller values of  $v'$ .

The MRCI results for  $\text{Si}_2^+$  shown in Table 5 are very similar to the CCSD(T) results shown in Table 4 for the ground and first excited state. The  $a^2\Pi_u$  state is calculated to lie 0.55 eV above the  $X^4\Sigma_g^-$  state of the ion at the MRCI/aug-cc-pV5Z level of theory. Addition of the multireference Davidson correction decreases this to 0.49 eV. The R/UCCSD(T)/cc-pV5Z result shown in Table 4, 0.53 eV, is in excellent agreement. As also shown in Figure 1, a second  $^2\Pi_u$  state ( $\dots 4\sigma_g^2 4\sigma_u^2 2\pi_u^3$  in a single-determinant formalism) lies about 0.8 eV above the  $a^2\Pi_u$  state. At short bond distances, i.e., less than 2.3 Å, these two  $^2\Pi_u$  states strongly interact and exhibit an avoided crossing near 2.2 Å. It should be noted that the MRCI+Q/aug-cc-pV5Z ionization potential of 7.87 eV is only slightly lower than the estimated CBS limit  $IP_e$  calculated at the R/UCCSD(T) level

**TABLE 8: Si<sub>2</sub> H<sup>3</sup>Σ<sub>u</sub><sup>-</sup>/Si<sub>2</sub><sup>+</sup> X<sup>4</sup>Σ<sub>g</sub><sup>-</sup> Vibrational State Overlaps from MRCI+Q/aug-cc-pV5Z Potential Energy Functions**

$v' \setminus v''$	0	1	2	3	4	5
0	0.005	0.018	0.045	0.091	0.155	0.230
1	-0.015	-0.048	-0.107	-0.187	-0.269	-0.327
2	0.031	0.090	0.178	0.266	0.313	0.280
3	-0.054	-0.141	-0.241	-0.299	-0.263	-0.122
4	0.084	0.194	0.281	0.273	0.139	-0.062
5	-0.119	-0.240	-0.288	-0.193	0.012	0.193

of 7.91 eV (see above). Using MRCI+Q/aug-cc-pV5Z potential energy functions, the nuclear motion contribution (vibrational) to the state overlaps between the Si<sub>2</sub> H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> and Si<sub>2</sub><sup>+</sup> X<sup>4</sup>Σ<sub>g</sub><sup>-</sup> states have been calculated using numerical<sup>35</sup> vibrational wave functions. These results are shown in Table 8.

## Discussion

Marijnissen and ter Meulen,<sup>16</sup> in obtaining the most accurate evaluation of the <sup>28</sup>Si<sub>2</sub> ionization potential, 63 884(7) cm<sup>-1</sup> = 7.9206 eV, have used the N<sup>3</sup>Σ<sub>u</sub><sup>-</sup> state of Si<sub>2</sub> at 46 763 cm<sup>-1</sup> as the intermediate state in their two-photon photoionization process. These authors have argued that this intermediate state is dominated by a single determinant ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup>5σ<sub>u</sub><sup>1</sup> electronic configuration which gives rise to the ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup> electronic configuration (X<sup>4</sup>Σ<sub>g</sub><sup>-</sup>) of the ground state of the ion. These arguments are indeed valid, although these authors did not consider that there is likely to be significant multireference character in the excited states of Si<sub>2</sub>.

Without consideration of the multireference character of the excited state wave functions, Marijnissen and ter Meulen<sup>16</sup> have argued that the bracketing of the Si<sub>2</sub> ionization potential between 7.90 and 8.08 eV by Winstead et al.<sup>15</sup> from resonant two-photon ionization spectroscopy is invalid and that their observed IP does not correlate to the ground state of the Si<sub>2</sub><sup>+</sup> ion but rather to an excited state. Marijnissen and ter Meulen argue that the H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> intermediate state accessed by Winstead et al. in their experiment arises from the ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>1</sup>2π<sub>g</sub><sup>1</sup> electronic configuration, whereas the X<sup>4</sup>Σ<sub>g</sub><sup>-</sup> ground state of the ion belongs to the ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup> electronic configuration. This suggests that ionization from the H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> state of Si<sub>2</sub> would require that two electrons change their molecular orbitals, a photoionization process with low probability. Furthermore, these authors<sup>16</sup> suggest that the H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> state correlates with the ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>1</sup> electronic excited state of Si<sub>2</sub><sup>+</sup> (i.e., the a<sup>2</sup>Π<sub>u</sub> state).

The results given in Table 6 demonstrate that the arguments of Marijnissen and ter Meulen are oversimplified due to their lack of consideration of the multireference character of the excited states of Si<sub>2</sub>. The validity of the single determinant model is placed in serious doubt if one simply surveys the plethora of Si<sub>2</sub> excited states calculated by Peyerimhoff and Buenker<sup>33</sup> in their early multireference study which clearly established that the possibility for excited state mixing is significant. It is somewhat surprising that Marijnissen and ter Meulen accepted the G2 results<sup>6</sup> for the first IP of Si<sub>2</sub> to form the ground state of the ion yet ignored the calculated energy difference of 0.42 eV for the difference in the energy of the ground and first excited <sup>2</sup>Π<sub>u</sub> state of Si<sub>2</sub><sup>+</sup>, especially in view of the good agreement between their determined value and the lower bound of Winstead et al.<sup>15</sup> One cannot easily invoke the existence of a very low-lying (<0.4 eV) excited state to explain the good agreement between these two photoionization results.

A possible source of error in the photoionization experiments of Winstead et al. would be that a different state other than the ground state of Si<sub>2</sub> was excited in their photoionization experiments. This possibility and the potential candidate A<sup>3</sup>Π<sub>u</sub>

state were certainly eliminated by the extensive spectroscopic study of Winstead et al.<sup>34</sup> on the H–X band system which demonstrated a clean <sup>3</sup>Σ<sub>u</sub><sup>-</sup> to <sup>3</sup>Σ<sub>g</sub><sup>-</sup> spectrum with no evidence for involvement of the A<sup>3</sup>Π<sub>u</sub> state in the cold expansion of Si<sub>2</sub> under the same conditions as used in the photoionization experiments.

A simple argument that can be evoked to explain the experimental results of Winstead et al.<sup>15</sup> is that the H state of Si<sub>2</sub> is not dominated by a single configuration to the exclusion of other configurations that would prevent coupling to the ground state of the ion. Whereas Table 6 clearly shows that the ground state of Si<sub>2</sub> is dominated by the single configuration, ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup>, the H state, as noted above, is composed of strongly mixed configurations. As well, its multireference character changes as a function of internuclear distance. The two configurations of greatest import to the two-photon ionization process through the H<sup>3</sup>Σ<sub>u</sub><sup>-</sup> state to form the ground state ion are ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>u</sub><sup>2</sup>5σ<sub>u</sub><sup>1</sup>, significant at both  $r \sim 2.3$  Å (vertical excitation region) and  $r \sim 2.7$  Å ( $r_e$  for the H state of Si<sub>2</sub>), and ...4σ<sub>g</sub><sup>2</sup>4σ<sub>u</sub><sup>2</sup>5σ<sub>g</sub><sup>1</sup>2π<sub>g</sub><sup>2</sup>5σ<sub>u</sub><sup>1</sup>, significant at  $r \sim 2.7$  Å. The former directly correlates with the ground state of the ion by loss of the 5σ<sub>u</sub><sup>1</sup> electron. At  $r \sim 2.3$  Å, this state has a coefficient of 0.22 and at the larger  $r \sim 2.7$  Å, it has an even larger coefficient, 0.36. The contributions of these configurations are sufficiently large so as to have a direct impact on the photoionization process in producing the ground state of the ion. It is perhaps also worth mentioning that the relative magnitudes of these coefficients are not strongly dependent on the choice of orbitals used in the MRCI. Test calculations using pseudocanonical orbitals optimized only for the ground electronic state resulted in CI coefficients nearly identical to those shown in Table 6.

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