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The Molecular Structure and Ionization Potential of Si₂: The Role of the Excited States in the Photoionization of Si₂

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The ionization potentials (IP) of Si₂ (X ³Σ_g[−]) to form the X ⁴Σ_g[−] and a²Π_u states of Si₂⁺ 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 ⁴Σ_g[−] ground state of the ion is 7.913 eV as compared to an experimental value of 7.9206 eV. The a²Π_u state is predicted to lie 0.52 eV above the X ⁴Σ_g[−] ground state of Si₂⁺. The 1 ³Δ_u, 2 ³Δ_u, H ³Σ_u[−], and K ³Σ_u[−] excited states of Si₂, as well as the X ⁴Σ_g[−], a²Π_u, and 2²Π_u states of Si₂⁺, 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 Si₂ 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 ⁴Σ_g[−] electronic state of Si₂⁺ 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.^{1–11} The discovery of emissive nanometer-scale silicon clusters has further heightened this interest.³ 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.^{12,13} Here we approach this description with chemically accurate calculations on the silicon dimer and its ion.

Si₂ has two low-lying states. The X ³Σ_g[−] ground state, corresponding to an orbital occupancy of ...4σ_g²4σ_u²5σ_g²2π_u², lies about 330 cm^{−1} below the first excited state, of ³Π_u symmetry and ...4σ_g²4σ_u²5σ_g¹2π_u³ occupancy. Both states have been the focus of high level calculations^{1,6} and experimental measurements.¹ Given the closeness of the two neutral states, the ground state of the Si₂⁺ cation could result from the removal of either a π or σ electron, resulting in a ²Π_u state

(...4σ_g²4σ_u²5σ_g²2π_u¹) or a ⁴Σ_g[−] state (...4σ_g²4σ_u²5σ_g¹2π_u²), respectively. It has been previously shown⁶ at the G2 level¹⁴ that the ground state of the ion is the ⁴Σ_g[−] state, with the ²Π_u state lying 9.6 kcal/mol (0.42 eV) higher in energy.

There have been several experimental determinations of the IP of Si₂. Trevor et al.¹⁰ determined a lower bound of 7.87 eV, while Fuke et al.² determined the ionization energy to be higher than 8.49 eV. More recently, Boo and Armentrout⁹ reported a value that was ≤8.04 eV, based on their measurement of the enthalpy of formation of Si₂⁺ and the JANAF enthalpy of formation of Si₂. Winstead et al.¹⁵ used mass-selected resonant two-photon ionization spectroscopy through the H ³Σ_u[−] 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 Meulen¹⁶ have used mass-selected photoionization spectroscopy through the intermediate N ³Σ_u[−] (~...4σ_g²4σ_u²5σ_g¹2π_u²5σ_u¹ in a single-determinant formalism) excited state of Si₂ to determine the adiabatic ionization energy of ²⁸Si₂ 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 ³Σ_u[−] (~...4σ_g²4σ_u²5σ_g²2π_u¹2π_g¹ in a single-determinant formalism) excited state of Si₂ 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.¹⁷ We have recently been calculating the thermodynamic properties of several silicon-containing molecules.¹⁷ⁱ Here, we report calculations on the spectroscopic properties and dissociation energies for the ground state and for several low-lying excited states of the Si₂ molecule relevant to the photoionization process. We also calculate the energies of the three lowest lying states of Si₂⁺. This study provides further confirmation of the ionization potential, the energetics of several excited states of Si₂ 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 Meulen¹⁶ in light of the result that many of the low-lying states of Si₂ are not well described by a single configuration.

Approach

Calculations on the ground state of Si₂ and on the two lowest lying states of Si₂⁺ 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)].¹⁸ The initial energetics were calculated within the frozen core (FC) approximation in which the 10 inner shell electrons (1s²2s²2p⁶) 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.¹⁹ 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 Si₂ the UCCSD(T) and R/UCCSD(T) methods produce energies that agree to within 0.0001 E_h. Spectroscopic constants were obtained via the usual Dunham²⁰ 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 ³Σ_g[−] ground state, the two lowest lying ³Δ_u states, and the two lowest lying ³Σ_u[−] 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 contracted²¹ 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_u symmetry (D_{2h} symmetry was used throughout). A similar treatment was also used for the positive ion. The orbitals were obtained in a state-averaged CASSCF (X ⁴Σ_g[−], ¹²Π_u, and ²²Π_u), and the MRCI calculations consisted of a separate calculation for the ground state and a two-state icMRCI for the ²Π_u states. The MRCI results were also corrected for higher order excitations through the use of the multireference Davidson “+Q” correction.²² Spectroscopic constants were

TABLE 1: UCCSD(T)(FC) Results for Si₂ (X ³Σ_g[−])

basis	D _e (kcal/mol)	R _e (Å)	ω _e (cm ^{−1})	ω _e x _e (cm ^{−1})	E (E _h)
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				−578.000021
CBS(aTQ5/mix)	75.61				−578.000030
CBS(aQ56/exp)	75.77				−578.000030
CBS(aQ56/mix)	75.58				−578.00005
expt ^a		2.246	510.98	2.02	

^a 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.²³ 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.¹⁷ 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-96/97²⁴ and Gaussian 94²⁵ 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.²⁶ 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:²⁷

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

In the study of Feller and Peterson,¹⁷ 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 set³⁶ 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 Si_2^a

molecule	CBS D_e	$1/2 \omega_e$ (aVQZ)	ΔE_{CV}^e	ΔE_{SR}^f	ΔE_{SO}^g	ΣD_0	IP (eV)	expt
$\text{Si}_2 (\text{X}^3\Sigma_g^-)^b$	75.6	0.74	0.5	−0.1	−0.9	74.4 ± 0.4		74.0^h
$\text{Si}_2^+ (\text{X}^4\Sigma_g^-)^c$	−106.59 ^d	0.68	0.2	−0.1	−0.9		7.913 (7.918) ^j	7.9206 eV ⁱ
$\text{Si}_2^+ (\text{a}^2\Pi_u)^e$	−118.83 ^d	0.56	0.1	−0.1	−0.9		8.443 (8.444) ^j	

^a Results are given in kcal/mol except for the ionization potentials which are given in eV. The total theoretical value is defined as: $E[\text{CCSD(T)}(\text{FC})/\text{CBS}] - 1/2\omega_e + \text{CV} + \text{scalar relativistic} + \text{atomic/molecular SO}$. ^b Calculated with the UCCSD(T) method. ^c Calculated with the R/UCCSD(T) method. ^d The negative value corresponds to the fact that Si_2^+ is unbound relative to two ground state Si atoms. ^e 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. ^f 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. ^g Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. ^h Reference 29. ⁱ Reference 16. ^j First value is CBS(aTQ5/mix) and the value in parentheses is CBS(aTQ5/exp).

TABLE 3: Si_2 Results from MRCI Calculations on the Ground State and Selected Excited States^a

	r_e (Å)	ω_e (cm ^{−1})	$\omega_e x_e$ (cm ^{−1})	E (E_h)	ΔE (eV)	ΔE (cm ^{−1})
aug-cc-pVTZ						
$\text{X}^3\Sigma_g^-$	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
$\text{H}^3\Sigma_u^-$	2.7041	261.8	1.87	−577.85955	2.965	23914
+Q	2.6776	272.0	1.72	−577.87955	2.852	22999
$\text{K}^3\Sigma_u^-$	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						
$\text{X}^3\Sigma_g^-$	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
$\text{H}^3\Sigma_u^-$	2.6888	264.9	1.79	−577.868842	3.013	24305
+Q	2.6606	276.0	1.73	−577.889472	2.900	23390
$\text{K}^3\Sigma_u^-$	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						
$\text{X}^3\Sigma_g^-$	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
$\text{H}^3\Sigma_u^-$	2.6803	267.9	1.80	−577.87194	3.034	24469
+Q	2.6520	279.3	1.76	−577.892794	2.920	23550
$\text{K}^3\Sigma_u^-$	2.3644	453.5	8.23	−577.841986	3.849	31044
+Q	2.3466	445.5	6.09	−577.861206	3.779	30483
expt ^b						
$\text{X}^3\Sigma_g^-$	2.246	510.98	2.02		0	0
$\text{H}^3\Sigma_u^-$	2.6427	279.28	1.99		2.9945	24151
$\text{K}^3\Sigma_u^-$	2.348	462.6	5.95		3.8180	30792

^a Rows labeled with +Q include the multireference Davidson correction. ^b Reference 29.

single and double excitations (CISD/cc-pVTZ).²⁸ 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 Si_2 are given in Tables 1 and 2. The multireference CI results for $\text{Si}_2 (\text{X}^3\Sigma_g^-)$,

$1^3\Delta_u$, $2^3\Delta_u$, $\text{H}^3\Sigma_u^-$, and $\text{K}^3\Sigma_u^-$) are given in Table 3. The R/UCCSD(T) results for the two lowest states of the ion Si_2^+ are given in Tables 2 and 4, while the MRCI results for Si_2^+ are shown in Table 5.

The calculated bond length for ground-state Si_2 using the aug-cc-pVQZ and higher basis sets are within 0.01 Å of the experimental value.²⁹ The remaining error is due primarily to core–valence correlation effects.³⁷ The frequencies calculated at the highest levels for the ground state are within 4 cm^{−1} of the experimental values.²⁹ 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 $X^4\Sigma_g^-$ and $a^2\Pi_u$ States of Si_2^+

	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	E_{min} (E _h)	E_{min} (E _h) augmented
$X^4\Sigma_g^-$					
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
$a^2\Pi_u$					
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

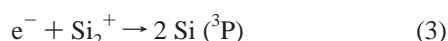
TABLE 5: Si_2^+ Results from MRCI Calculations on the Ground State and Selected Excited States^a

	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)	E (E _h)	ΔE (eV) ^b
aug-cc-pV5Z					
$X^4\Sigma_g^-$	2.2742	471.8	2.49	-577.7013634	7.675
+Q	2.2745	470.1	2.52	-577.7107371	7.874
$a^2\Pi_u$	2.4546	385.3	1.55	-577.681062	8.228
+Q	2.4503	387.5	1.72	-577.692666	8.366
$2^2\Pi_u$	2.2218	627.1	11.99	-577.652346	9.009
+Q	2.2162	607.2	7.45	-577.662566	9.185

^a Rows labeled with +Q include the multireference Davidson correction. ^b 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.³⁰ Knudsen cell/third law measurements on the Si-Si₂ equilibrium yield D_0 values of 73.3, 74.3, and 70.4 kcal/mol (average = 72.7 kcal/mol).³¹ The CCSD(T)/CBS value of $D_0(Si_2) = 74.4 \pm 0.4$ kcal/mol calculated in this study is at the high end of these values³⁰⁻³² but in good agreement with the 74.0 kcal/mol, which is based on several experimental measurements, recommended by Huber and Herzberg.²⁸

The contribution of the electronic energy to the adiabatic ionization potential for the ground state of Si_2 ($^3\Sigma_g^-$) 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_2^+ 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 ± 0.02 eV for $Si_2(X^3\Sigma_g^-)$ to form $Si_2^+(X^4\Sigma_g^-)$. This value is in excellent agreement with the experimental value of 7.9206(9) eV.¹⁶ The G2 value⁶ of 7.94 eV for the $X^4\Sigma_g^-$ 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 $a^2\Pi_u$ state is calculated to be 8.443 eV, with the two extrapolation procedures differing by only 0.001 eV. For the $a^2\Pi_u$ 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 $Si_2(X^3\Sigma_g^-)$ to form $Si_2^+(a^2\Pi_u)$ is 8.44 ± 0.02 eV. Thus, the $a^2\Pi_u$ state of the cation is predicted to lie 0.52 eV above the $X^4\Sigma_g^-$ state.

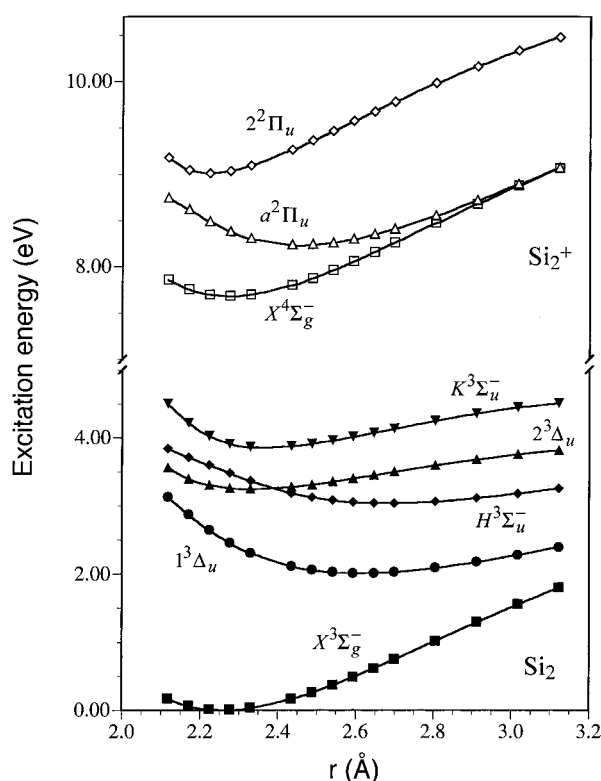
Because the calculated bond distance for the ground state of Si_2 , 2.255 Å, is very similar to the value predicted for the ground state of $Si_2^+(X^4\Sigma_g^-)$, 2.267 Å, the vertical and adiabatic ionization potentials will be very similar. However, the calculated bond distance for the $Si_2^+ a^2\Pi_u$ state is significantly longer at 2.451 Å. Thus, vertical ionization to the $a^2\Pi_u$ state is expected to require an additional 0.28 eV energy increment. We note that the G2 value⁶ of 8.36 eV for the adiabatic IP of the $a^2\Pi_u$ state is in reasonable agreement with our calculated value at the CBS limit.

The calculated spectroscopic parameters for the excited $1^3\Delta_u$, $2^3\Delta_u$, $H^3\Sigma_u^-$, and $K^3\Sigma_u^-$ states of Si_2 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 ΔE 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 , ω_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, ω_e within 11 cm⁻¹, and ΔE within 0.04 eV. At the MRCI+Q level, the bond distance is within 0.01 Å, ω_e within 1 cm⁻¹, and ΔE within 0.07 eV. Thus, we are able to reliably reproduce the parameters of the $H^3\Sigma_u^-$ 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 ΔE within 0.04 eV. The results presented in Table 3 for the excited states of Si_2 are the most accurate available to date.

In Table 6, we summarize the dominant reference configurations for the calculated excited states of Si_2 . Not surprisingly, we note that the excited states of Si_2 have significant multireference character. This is especially true for the $2^3\Delta_u$, $H^3\Sigma_u^-$, and $K^3\Sigma_u^-$ states. Our ability to accurately calculate the spectroscopic parameters of the $H^3\Sigma_u^-$ and $K^3\Sigma_u^-$ states of Si_2 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 Si₂ Based on MRCI Calculations

state		coefficient	excitation	configuration
X ³ Σ _g ⁻	r _e (X)	0.913		4σ _g ² 4σ _u ² 5σ _g ² 2π _u ²
		0.117	2π _u ² → 2π _g ²	4σ _g ² 4σ _u ² 5σ _g ² 2π _g ²
1 ³ Δ _u	vertical	0.891	2π _u ² → 2π _u ¹ 2π _g ¹	4σ _g ² 4σ _u ² 5σ _g ² 2π _u ¹ 2π _g ¹
		0.243	5σ _g ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 4σ _u ² 2π _u ³ 2π _g ¹
2 ³ Δ _u	vertical	0.857	5σ _g ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 4σ _u ² 2π _u ³ 2π _g ¹
		0.236	2π _u ² → 2π _u ¹ 2π _g ¹	4σ _g ² 4σ _u ² 5σ _g ² 2π _u ¹ 2π _g ¹
		0.168	5σ _g ² 2π _u ² → 2π _u ¹ 2π _g ³	4σ _g ² 4σ _u ² 2π _u ¹ 2π _g ³
H ³ Σ _u ⁻	vertical	0.163	4σ _u ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 5σ _g ² 2π _u ³ 2π _g ¹
		0.636	2π _u ² → 2π _u ¹ 2π _g ¹	4σ _g ² 4σ _u ² 5σ _g ² 2π _u ¹ 2π _g ¹
		0.608	5σ _g ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 4σ _u ² 2π _u ³ 2π _g ¹
		0.218	5σ _g ² → 5σ _g ¹ 5σ _u ¹	4σ _g ² 4σ _u ² 5σ _g ¹ 5σ _u ¹ 2π _u ² 5σ _u ¹
H ³ Σ _u ⁻	~r _e (H)	0.778	2π _u ² → 2π _u ¹ 2π _g ¹	4σ _g ² 4σ _u ² 5σ _g ² 2π _u ¹ 2π _g ¹
		0.270	5σ _g ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 4σ _u ² 2π _u ³ 2π _g ¹
		0.362	5σ _g ² → 5σ _g ¹ 5σ _u ¹	4σ _g ² 4σ _u ² 5σ _g ¹ 5σ _u ¹ 2π _u ² 5σ _u ¹
K ³ Σ _u ⁻	vertical	0.175	5σ _g ² 2π _u ² → 5σ _g ¹ 5σ _u ¹ 2π _u ²	4σ _g ² 4σ _u ² 5σ _g ¹ 5σ _u ¹ 2π _u ²
		0.651	5σ _g ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 4σ _u ² 2π _u ³ 2π _g ¹
		0.571	2π _u ² → 2π _u ¹ 2π _g ¹	4σ _g ² 4σ _u ² 5σ _g ² 2π _u ¹ 2π _g ¹
		0.211	5σ _g ² → 5σ _g ¹ 5σ _u ¹	4σ _g ² 4σ _u ² 5σ _g ¹ 5σ _u ¹ 2π _u ² 5σ _u ¹
		0.153	4σ _u ² 2π _u ² → 2π _u ³ 2π _g ¹	4σ _g ² 5σ _g ² 2π _u ³ 2π _g ¹

**Figure 1.** Ground and excited state curves for Si₂ and Si₂⁺ calculated at the MRCI/aug-cc-pV5Z level of theory. Note that addition of the multireference Davidson correction (+Q) shifts the Si₂⁺ states by about +0.1 eV relative to the Si₂ ground state.

multireference nature of the H ³Σ_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 ³Σ_u⁻ state has significant implications for the experimental determination of the Si₂ 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: Si₂ H³Σ_u⁻ ← X³Σ_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^a

<i>v''v'</i>	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

^a 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 calculated³⁵ 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 Si₂⁺ shown in Table 5 are very similar to the CCSD(T) results shown in Table 4 for the ground and first excited state. The a²Π_u state is calculated to lie 0.55 eV above the X⁴Σ_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 ²Π_u state (...4σ_g²4σ_u²2π_u³ in a single-determinant formalism) lies about 0.8 eV above the a²Π_u state. At short bond distances, i.e., less than 2.3 Å, these two ²Π_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: Si₂ H³Σ_u⁻/Si₂⁺ X⁴Σ_g⁻ Vibrational State Overlaps from MRCI+Q/aug-cc-pV5Z Potential Energy Functions

$v'' \backslash v'$	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 Si₂ H³Σ_u⁻ and Si₂⁺ X⁴Σ_g⁻ states have been calculated using numerical³⁵ vibrational wave functions. These results are shown in Table 8.

Discussion

Marijnissen and ter Meulen,¹⁶ in obtaining the most accurate evaluation of the ²⁸Si₂ ionization potential, 63 884(7) cm⁻¹ = 7.9206 eV, have used the N³Σ_u⁻ state of Si₂ at 46 763 cm⁻¹ 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_g²4σ_u²5σ_g¹2π_u²5σ_u¹ electronic configuration which gives rise to the ...4σ_g²4σ_u²5σ_g¹2π_u² electronic configuration (X⁴Σ_g⁻) 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 Si₂.

Without consideration of the multireference character of the excited state wave functions, Marijnissen and ter Meulen¹⁶ have argued that the bracketing of the Si₂ ionization potential between 7.90 and 8.08 eV by Winstead et al.¹⁵ from resonant two-photon ionization spectroscopy is invalid and that their observed IP does not correlate to the ground state of the Si₂⁺ ion but rather to an excited state. Marijnissen and ter Meulen argue that the H³Σ_u⁻ intermediate state accessed by Winstead et al. in their experiment arises from the ...4σ_g²4σ_u²5σ_g²2π_u¹2π_g¹ electronic configuration, whereas the X⁴Σ_g⁻ ground state of the ion belongs to the ...4σ_g²4σ_u²5σ_g¹2π_u² electronic configuration. This suggests that ionization from the H³Σ_u⁻ state of Si₂ would require that two electrons change their molecular orbitals, a photoionization process with low probability. Furthermore, these authors¹⁶ suggest that the H³Σ_u⁻ state correlates with the ...4σ_g²4σ_u²5σ_g²2π_u¹ electronic excited state of Si₂⁺ (i.e., the a²Π_u 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 Si₂. The validity of the single determinant model is placed in serious doubt if one simply surveys the plethora of Si₂ excited states calculated by Peyerimhoff and Buenker³³ 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 results⁶ for the first IP of Si₂ 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 ²Π_u state of Si₂⁺, especially in view of the good agreement between their determined value and the lower bound of Winstead et al.¹⁵ 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 Si₂ was excited in their photoionization experiments. This possibility and the potential candidate A³Π_u

state were certainly eliminated by the extensive spectroscopic study of Winstead et al.³⁴ on the H–X band system which demonstrated a clean ³Σ_u⁻ to ³Σ_g⁻ spectrum with no evidence for involvement of the A³Π_u state in the cold expansion of Si₂ 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.¹⁵ is that the H state of Si₂ 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 Si₂ is dominated by the single configuration, ...4σ_g²4σ_u²5σ_g²2π_u², 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 H³Σ_u⁻ state to form the ground state ion are ...4σ_g²4σ_u²5σ_g¹2π_u²5σ_u¹, significant at both $r \sim 2.3$ Å (vertical excitation region) and $r \sim 2.7$ Å (r_e for the H state of Si₂), and ...4σ_g²4σ_u²5σ_g¹2π_g²5σ_u¹, significant at $r \sim 2.7$ Å. The former directly correlates with the ground state of the ion by loss of the 5σ_u¹ 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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